PHOTOCYCLOADDITION AND ELIMINATION REACTIONS

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conditions governing candidates for the degree of

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by

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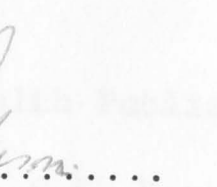
Canberra, A.C.T.

AUTHOR'S STATEMENT

All the research described in this thesis is my own work, except where specific reference is made to the contributions of others.



August 1967

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I would also like to thank the Commonwealth Public Service Board for the award of a Part-Time Free Place, Dr. C.S. Barnes for the measurement of the mass spectra, Dr. T. Batterham, for the measurement of the n.m.r. $C^{13}H$ satellite spectra, and members of the Department of Chemistry for their advice and assistance.

Finally, I wish to express my appreciation of my wife, Enid, who not only endured, but also assisted.

CONTENTS

NOTE

Owing to the fact that the mass spectral figures used in Section 4 had been prepared for another purpose than this thesis, certain compounds mentioned in Section 4, Mass Spectral Studies, have been assigned chemical names which differ from those used in the remainder of the text. For example, cis-3,4-dichloro-cyclobut-1-ene* is used in Section 4, and cis 1,2 dichloro-cyclobut-3-ene is used elsewhere. N-phenyl cyclobutene-cis-3,4-dicarboximide is used in Section 4, while N-phenyl cyclobut-3-ene 1,2 dicarboximide* is used elsewhere. The names which are asterisked are the more correct assignments according to our interpretation of the I.U.P.A.C. nomenclature rules.

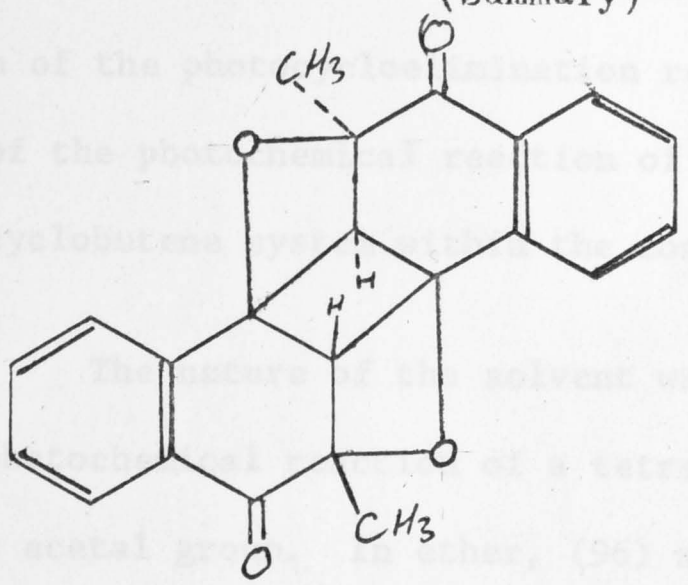
SUMMARY

An interest in the configuration of the photo-dimer of 2-methyl-1,4-naphthoquinone (1) led to an attempt to synthesise model compounds of known, unambiguous stereochemistry, which were to be used to prepare dimethyl cyclobutane tetracarboxylic acid derivatives. 1,2-dimethyl-cyclohex-3,5-diene-1,2-dicarboxylic anhydride (56) was prepared, and photolysed in solution, to give in low yield a mixture of syn, and anti-bicyclo (2,2,0) hexene valence isomers. The major product was o-xylene. Model compounds, containing substituted cyclobutane systems, were made for purposes of comparison with the photodimer of (1) utilising n.m.r. spectroscopic $C^{13}H$ technique. On the basis of current knowledge a double-oxetan structure (145) for the photo-dimer, cannot be excluded.

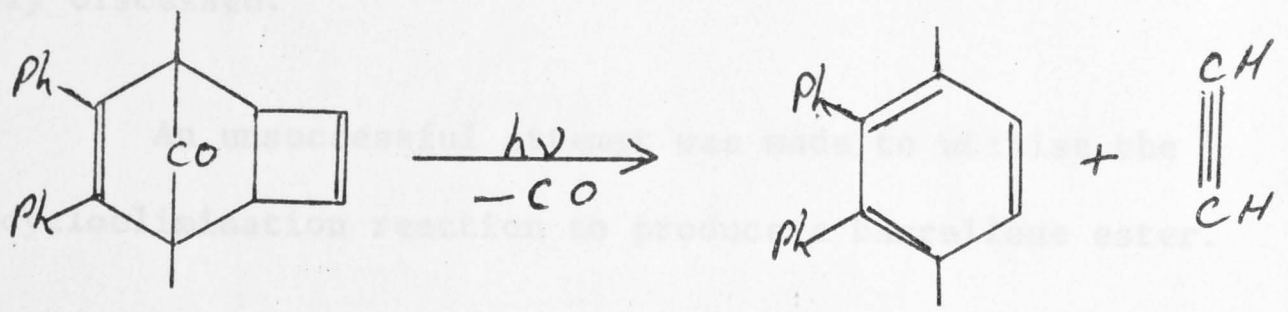
An initial investigation was made into other photo-cycloaddition reactions of (1) with compounds containing unsaturated bonds.

The interest in photocycloaddition and elimination reactions led to the preparation of compounds containing cyclobutane, or cyclobutene, systems. These compounds were photolysed in solution when it was found that the derivatives containing a bridge carbonyl group underwent a photoaromatisation, and a photocycloelimination reaction with cleavage of the cyclobutane, or cyclobutene ring. For example, the derivative (80) underwent the photolytic reaction shown

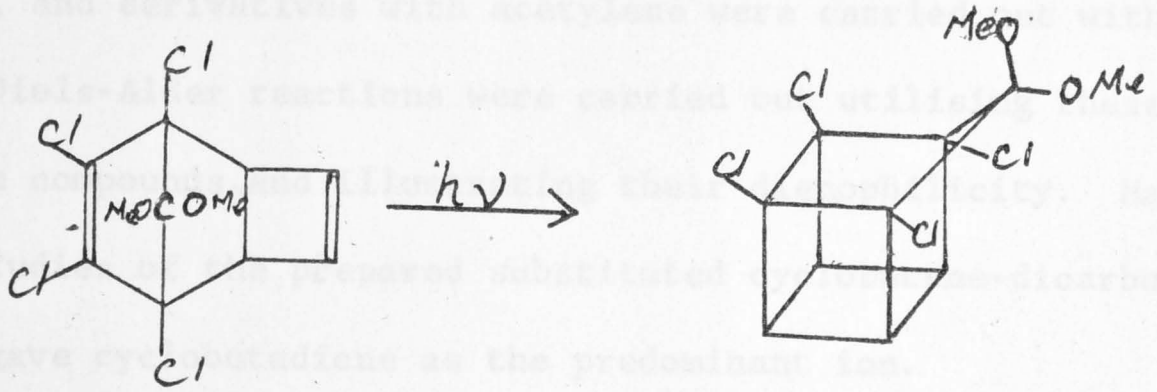
DIAGRAM A
(Summary)



(145)



(80) (78) (71)



(96) (110)

in Diagram A. It was found that the nature of the solvent influenced the path of the photocycloelimination reaction. The influence on the course of the photochemical reaction of an endo, or exo configuration of the cyclobutene system within the compound is discussed.

The nature of the solvent was found to influence the path of the photochemical reaction of a tetrachloro compound (96) containing a bridge acetal group. In ether, (96) may have formed a dimer with some dechlorination also. In acetone, (96) cycloadded intramolecularly to give a cage compound (110). Solvent-triplet sensitisation is briefly discussed.

An unsuccessful attempt was made to utilise the photocycloelimination reaction to produce a barrellene ester.

Low temperature photocycloaddition reactions of maleic anhydrides, and derivatives with acetylene were carried out with some success. Diels-Alder reactions were carried out utilising these cyclobutene compounds, and illustrating their dienophilicity. Mass spectral studies of the prepared substituted cyclobutene-dicarboximide compounds gave cyclobutadiene as the predominant ion.

SECTION 1

GENERAL INTRODUCTION

The study of the photochemistry of the compound menadione, or 2-methyl-1, 4-naphthoquinone (1) was initiated by an interest in the photochemical impairment of its vitamin K activity. This photochemical impairment is a problem in Australia where sunlight is more actinic than sunlight in Europe.

Madinaveitia[1] first reported in 1933 that the menadione (1) formed a photo-product upon exposure to sunlight. He suggested that it was dimeric and assigned the following structure: 2,3,2′,3′-tetrahydro-2,3-dimethyl-2,3,2′,3′-binaphthylene-1,4,1′,4′-tetrone.

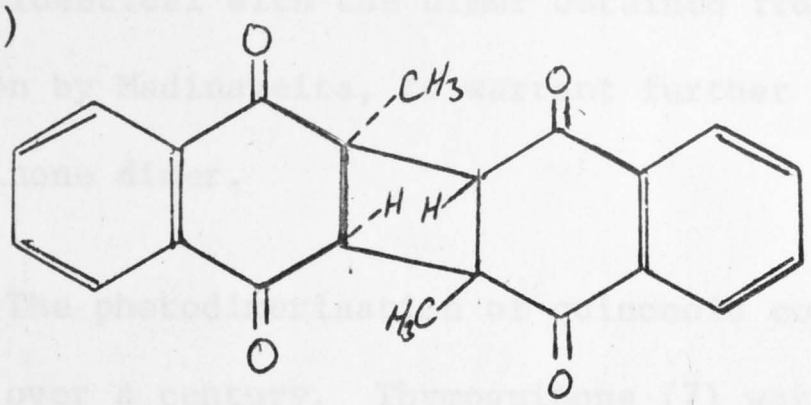
Yutaka Asahi[2] reported the isolation of 2 dimers of (1), obtained by the irradiation of (1) in dilute ethanolic solution in the presence of oxygen. These two dimers were obtained through the intermediary 2-methyl-3,4-epoxy-1,4-naphthoquinone (2) formed during the irradiation. He assigned the structures shown in Diagrams 1a and 1b.

Excluding <u>trans</u>-fused ring structures there are four possible isomers of the dimer depending on the positions of the two methyl groups in the cyclobutane ring, and the manner in which the naphthoquinonoid moieties are attached to the ring. These isomers can have the two methyls in the positions <u>cis</u>-1,2-, <u>cis</u>-1,3-, <u>trans</u>-1,2-, and <u>trans</u>-1,3-dimethyl respectively. These are shown in Diagram 1.

There was sufficient doubt on the basis of the assigned structures, and also on the different irradiation procedure in

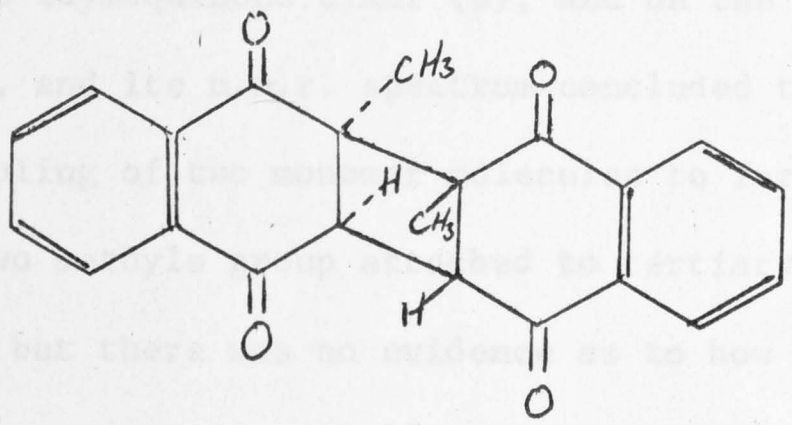
DIAGRAM 1

(a)



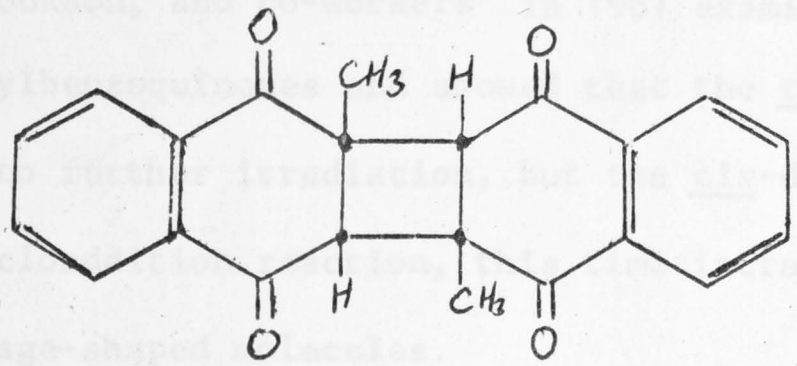
(3)

(b)



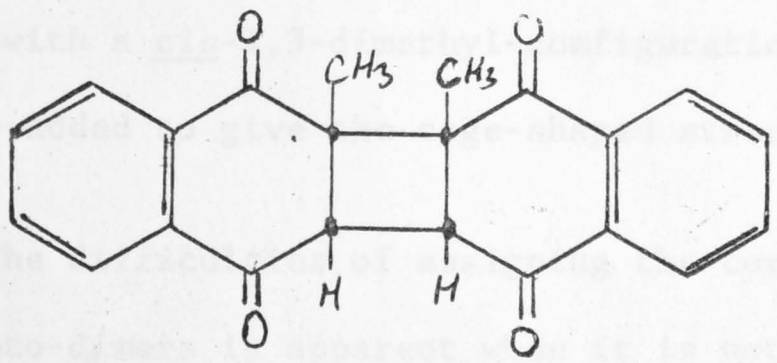
(4)

(c)



(5)

(d)



(6)

ethanol, as to whether one of the two dimers obtained by Yutaka Asahi was identical with the dimer obtained from the solid state irradiation by Madinaveita, to warrant further study on the 2-methyl naphthoquinone dimer.

The photodimerisation of quinonoid compounds has been known for over a century. Thymoquinone (7) was observed, in 1857, to form a dimeric compound on exposure to light.[3] Zavarin[4] in 1958, studied the thymoquinone dimer (8), and on the basis of its chemical properties, and its n.m.r. spectrum concluded that it had been formed by the coupling of two monomer molecules to form a cyclobutane ring with the two methyls group attached to tertiary carbon atoms in the dimer, but there was no evidence as to how the two monomer molecules were joined spatially in the cyclobutane ring.

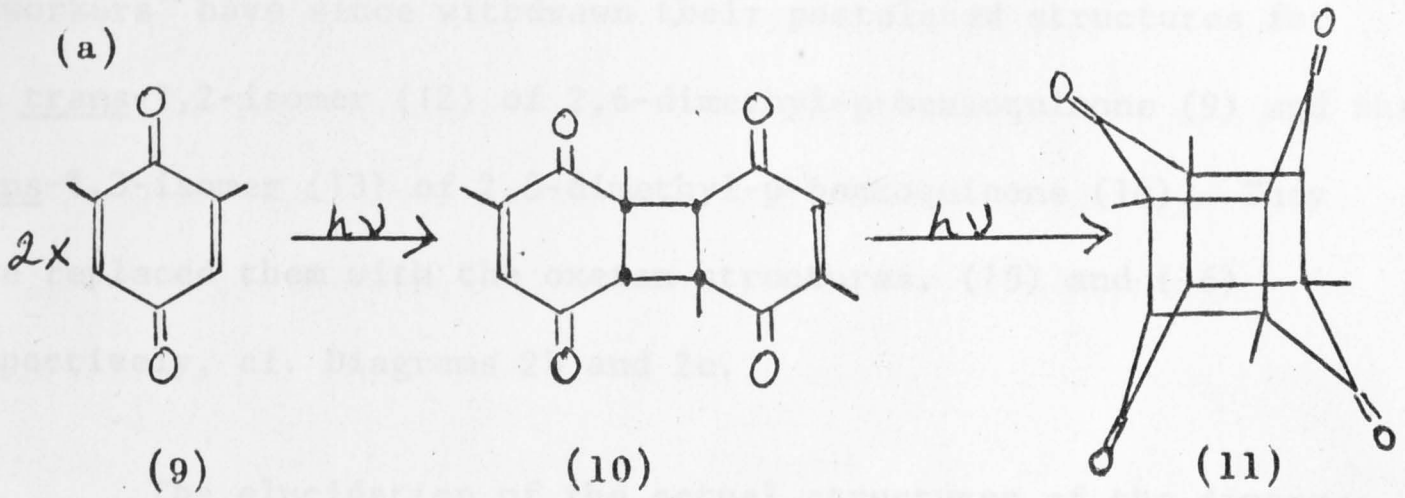
Cookson, and co-workers[5] in 1961 examined the photodimers of some alkylbenzoquinones and showed that the trans-dimers obtained are stable to further irradiation, but the cis-dimers obtained undergo a second cycloaddition reaction, this time intramolecularly to give saturated cage-shaped molecules.

For example, 2,6-dimethyl benzoquinone (9) gave a photo-dimer (10) with a cis-1,3-dimethyl-configuration which further photo-cyclo-added to give the cage-shaped structure (11). Diagram 2a.

The difficulties of assigning the correct steric structure to such photo-dimers is apparent when it is noted that Cookson and

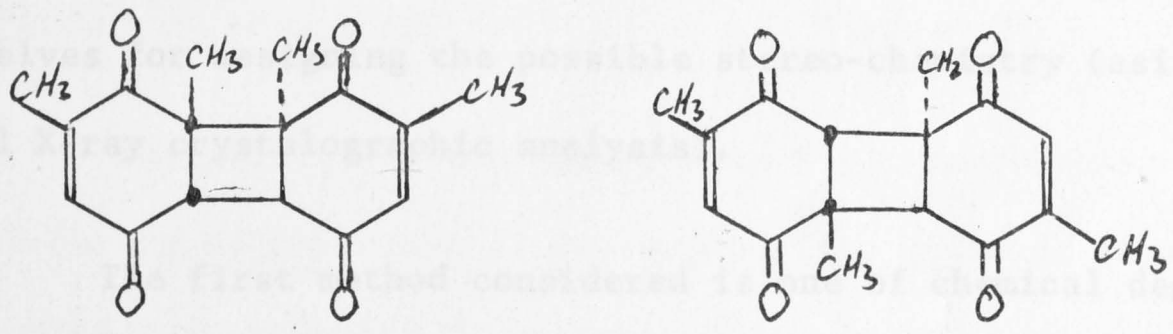
DIAGRAM 2

(a)



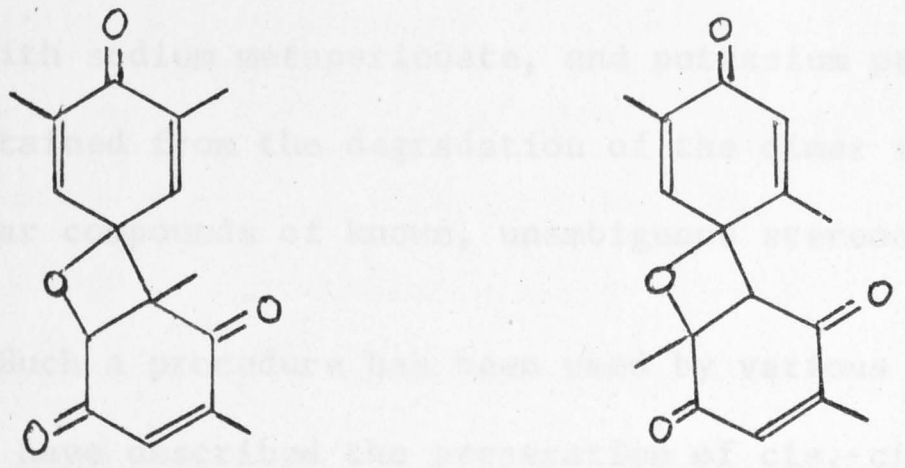
(9) (10) (11)

(b)



(12) (13)

(c)



(15) (16)

co-workers[6] have since withdrawn their postulated structures for the trans-1,2-isomer (12) of 2,6-dimethyl-p-benzoquinone (9) and the trans-1,3-isomer (13) of 2,5-dimethyl-p-benzoquinone (14). They have replaced them with the oxetan structures, (15) and (16) respectively, cf. Diagrams 2b and 2c.

The elucidation of the actual structures of the dimers is therefore not a simple problem, but two main methods present themselves for assigning the possible stereo-chemistry (aside from a full X-ray crystalographic analysis).

The first method considered is one of chemical degradation, where the outer structure of the dimer is removed to leave a much simpler, substituted cyclobutane ring system. This can be achieved by various oxidative techniques, including ozonolysis, or oxidative cleavage with sodium metaperiodate, and potassium permanganate. The product obtained from the degradation of the dimer is then compared with similar compounds of known, unambiguous stereochemistry.

Such a procedure has been used by various workers. Griffin and Veber[7] have described the preparation of cis,-cis,-cis-1,2,3,4-tetracarbomethoxy cyclobutane (17) from β-heptacyclene (18), a dimer of acenaphthylene (19) with a cis-orientation, and also the preparation of a cis, trans, cis-1,2,3,4-tetracarbomethoxy cyclobutane (20) from α-heptacyclene (21) which is a dimer of (19) with a trans-orientation. These reactions were carried out by ozonolysis of the dimer (19) and esterification of the resultant tetracarboxylic acid compounds.

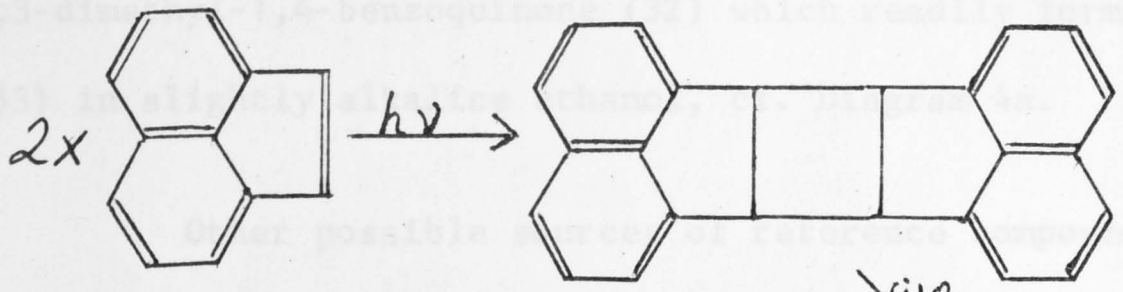
Diagram 3a illustrates the procedure used. The other two isomers have also been synthesised by Griffin and co-workers.[8] Criegee[9] has obtained three of the four possible isomers of the cyclobutane-1,2,3,4-tetracarboxylic acids by ozonolysis of cinnamic acid dimers, truxillic acids, (22) of known stereochemistry. The three isomers obtained are shown in Diagram 3b. Criegee[10] has also reported the preparation of trans-cyclobutane-bis anhydride (26) from the irradiation of maleic anhydride (27), cf. Diagram 3c.

The problem in the use of this first approach to elucidate the structure of the dimer of (1) was to find suitable precursors from which to synthesise these substituted cyclobutane reference compounds. One source was the alkylbenzoquinone dimers studied by Cookson. It was envisaged that these could possibly be converted to cis-1,3-dimethyl-cyclobutane -1,2,3,4-tetracarboxylic-cis-1,2,3,4-dianhydride (28), and the cis-2,3-dimethyl-cyclobutane-1,2,3,4-tetracarboxylic cis-1,2,3,4-dianhydride (29), cf. Diagram 3d. The trans-1,3-dimethyl cyclobutane-1,2,3,4-tetracarboxylic-trans-1,2,3,4-dianhydride (30) could perhaps be obtained from the thymoquinone dimer (8) which has been suggested to have the trans-configuration.[5]

Since the structure of (8) is in doubt, and since Cookson withdrew the dimer structures (12), and (13), the range of quinone dimers that can be used as precursors is restricted. The quinone dimers have a tendency to enolise, although this applies especially to those dimers whose cyclobutane rings have no methyl groups. This

DIAGRAM 3

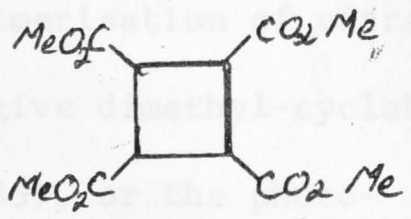
(a)



(19) (21)

(18) cis, β;

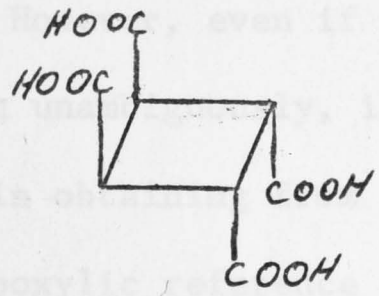
(21) trans, α.



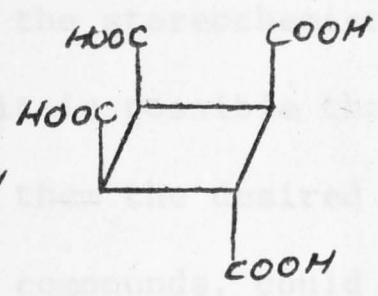
(17) cis, cis, cis;

(20) cis, trans, cis.

(b)



(23)



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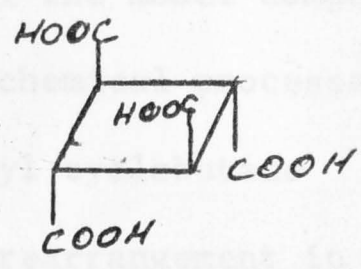
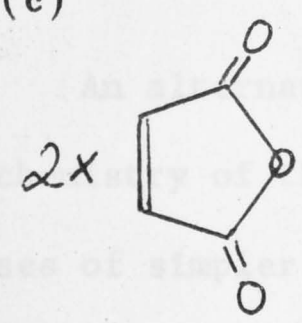


(25)

(c)



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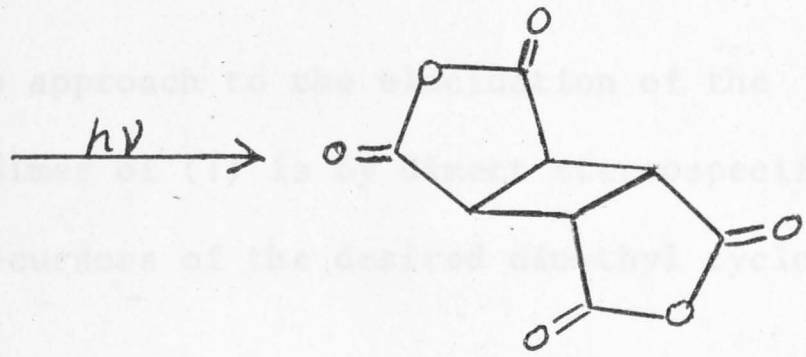
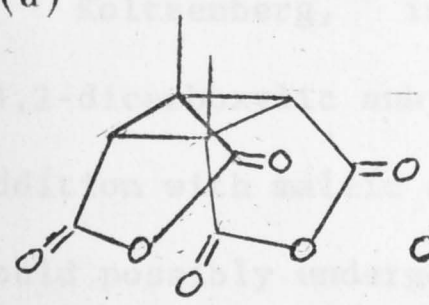


(26)

(d)



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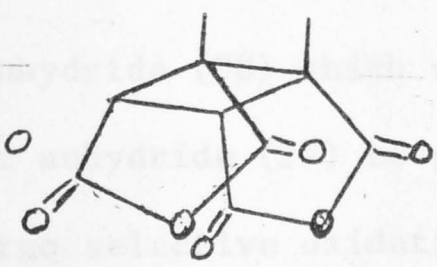

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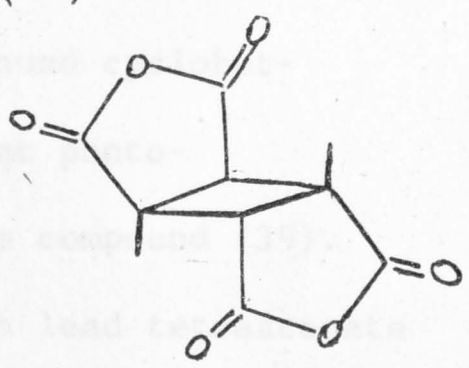


(30)

was shown by Cookson and co-workers[11] with the photo dimer (31) of 2,3-dimethyl-1,4-benzoquinone (32) which readily formed the quinol (33) in slightly alkaline ethanol, cf. Diagram 4a.

Other possible sources of reference compounds are cyclo-addition reactions which yield products with dimethyl-substituted cyclobutane ring systems. Examples are the dimerisation of citranconic anhydride (34) by ultraviolet irradiation to give dimethyl-cyclobutane 1,2,3,4-tetracarboxylic-1,2,3,4-dianhydride (35), or the photo-cycloaddition of duroquinone (36) with acenaphthylene described by Schenck and co-workers[12] to give the compound (37), cf. Diagram 4b.

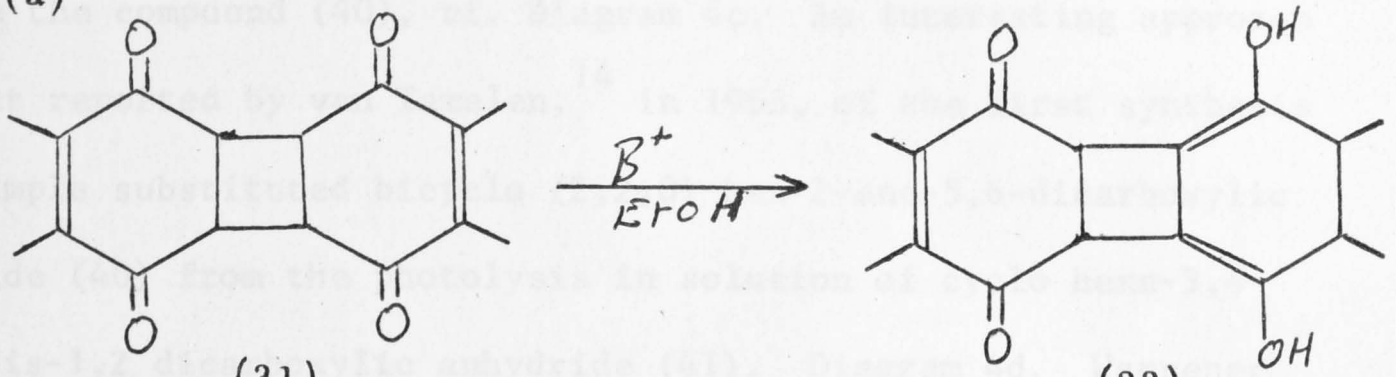
However, even if the stereochemistries of the model compounds were known unambiguously, it is possible that the chemical processes involved in obtaining from them the desired dimethyl cyclobutane tetra-carboxylic reference compounds, could cause rearrangement in the substituted cyclobutane systems.

An alternative approach to the elucidation of the stereochemistry of the dimer of (1) is by direct stereospecific syntheses of simpler precursors of the desired dimethyl cyclobutane systems.

Koltzenberg,[13] in 1966, reported the compound cyclobut-3-ene 1,2-dicarboxylic anhydride (38) which underwent photo-cycloaddition with maleic anhydride (27) to give the compound (39). This could possibly undergo selective oxidation with lead tetraacetate

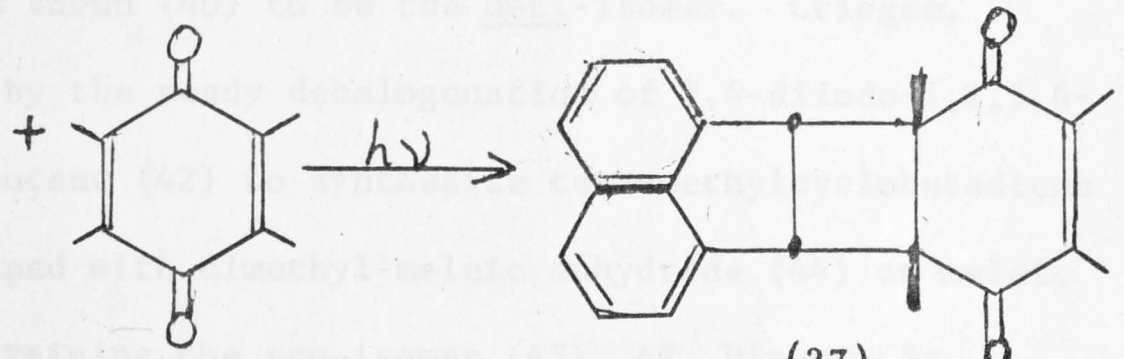
DIAGRAM 4.

(a)



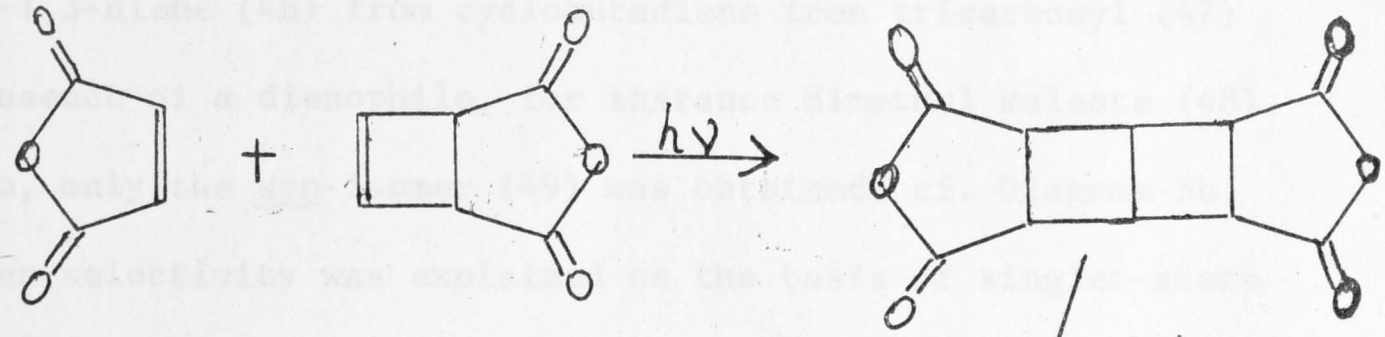
(31) (33)

(b)



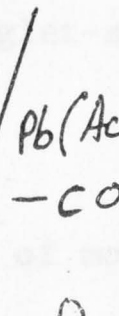
(19) (36) (37)

(c)

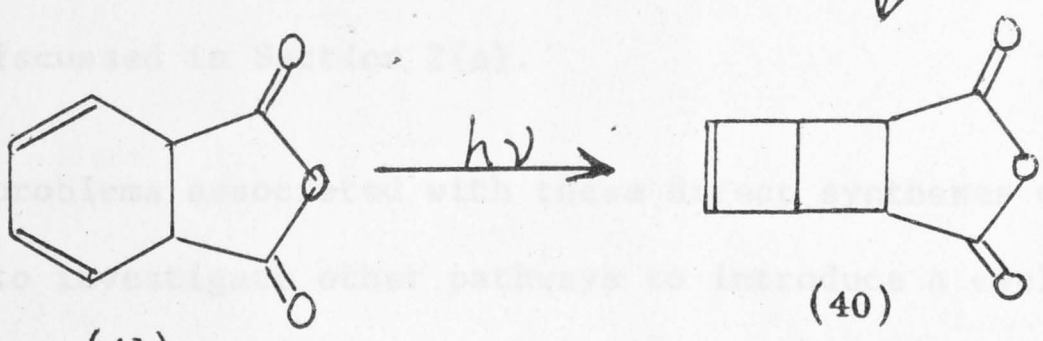


(27) (38)

(39)



(d)



(41) (40)

to give the compound (40), cf. Diagram 4c. An interesting approach was that reported by van Tamelen,[14] in 1963, of the first synthesis of a simple substituted bicyclo (2,2,0) hex-2-ene-5,6-dicarboxylic anhydride (40) from the photolysis in solution of cyclo hexa-3,4-diene-cis-1,2 dicarboxylic anhydride (41). Diagram 4d. Warrener and Bremner[15] have shown (40) to be the anti-isomer. Criegee,[16] in 1965, was able by the ready dehalogenation of 3,4-diiodo-1,2,3,4-tetramethyl cyclobutane (42) to synthesise tetramethylcyclobutadiene (43) which he trapped with dimethyl-maleic anhydride (44) or maleic anhydride (27), obtaining the syn-isomer (45), cf. Diagram 5a. Pettit,[17] synthesised a number of bicyclic compounds by generating cyclobuta-1,3-diene (46) from cyclobutadiene iron tricarbonyl (47) in the presence of a dienophile, for instance dimethyl maleate (48). Here, also, only the syn-isomer (49) was obtained, cf. Diagram 5b. This stereo-selectivity was explained on the basis of singlet-state cyclobutadiene.

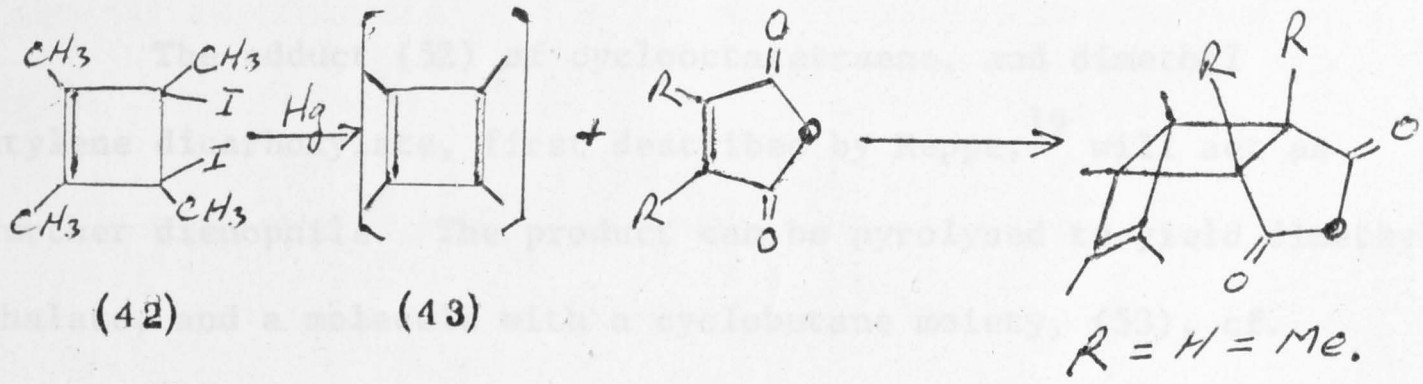
The direct approach of stereospecific synthesis of model compounds is discussed in Section 2(a).

The problems associated with these direct syntheses were an inducement to investigate other pathways to introduce a cyclobutane moiety into a molecule in much the same way as Pettit and co-workers' cyclobutadiene cycloaddition reaction.

Cis-3,4-dichloro-cyclobut-1-ene (50) has been used as a dienophile by Avram and co-workers,[18] and the product dechlorinated

DIAGRAM 5

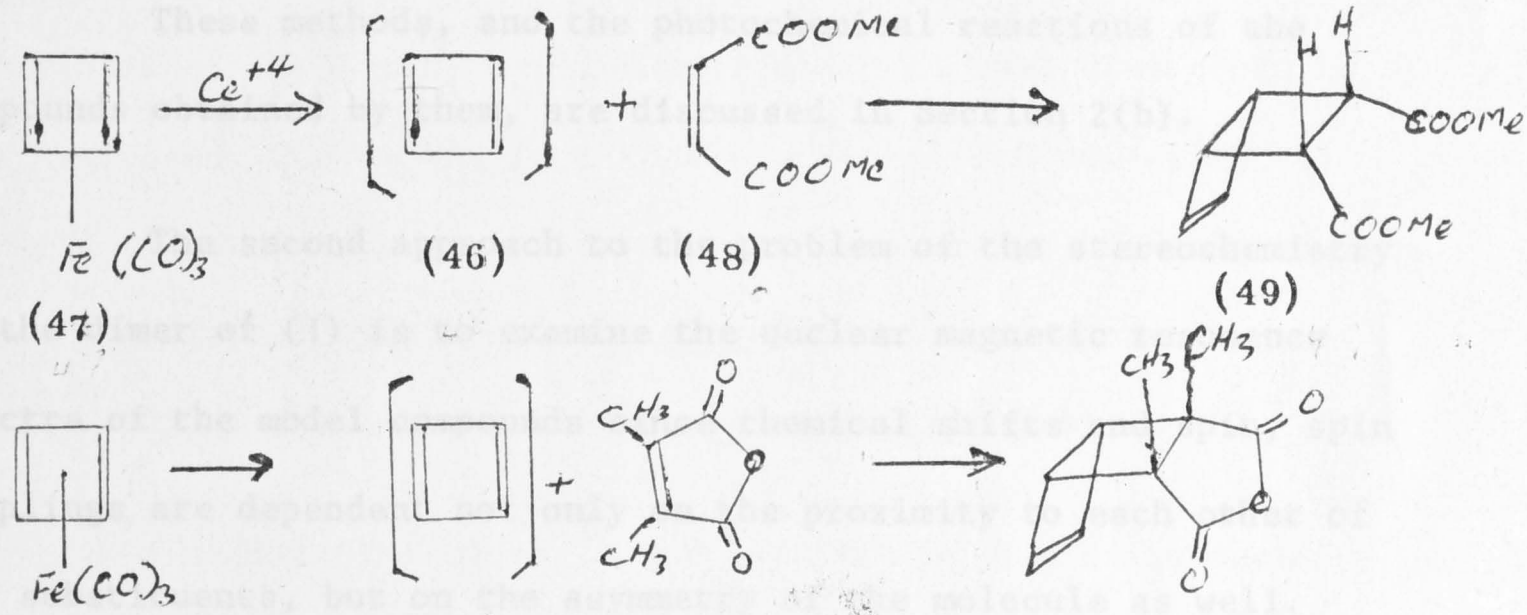
(a)



(42) (43) (45)

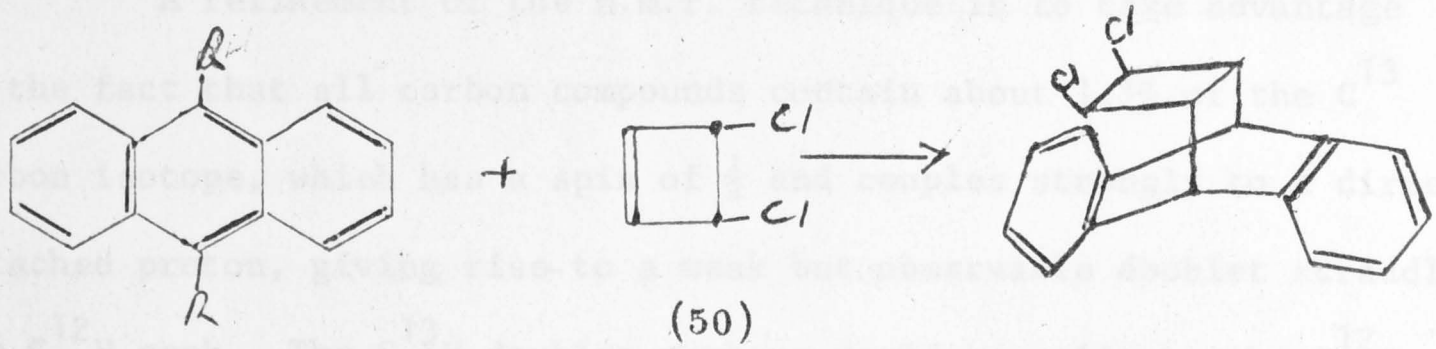
R = H = Me.

(b)



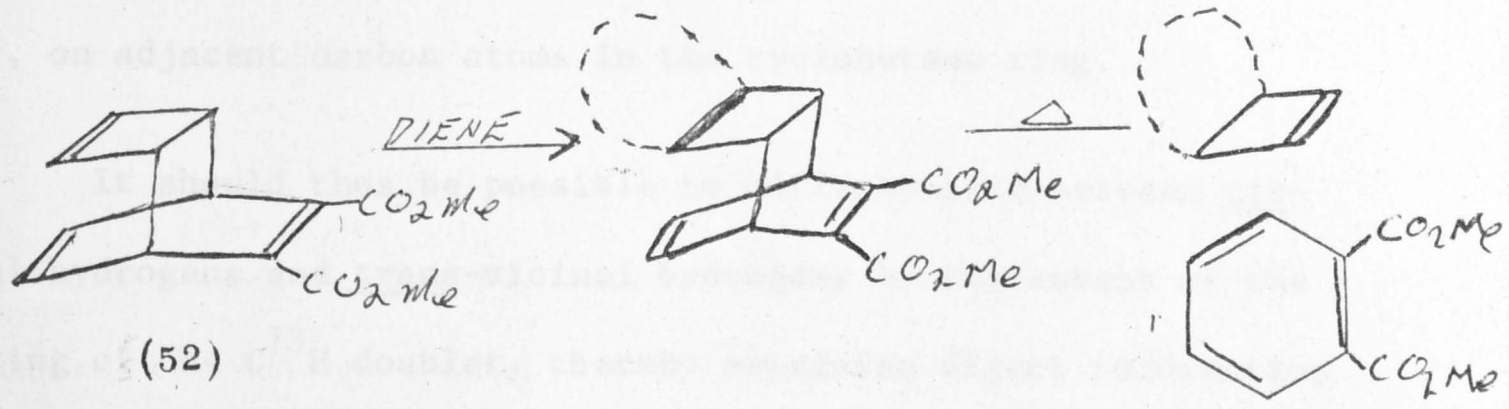
(47) (46) (48) (49)

(c)



(50)

(d)



(52)

to give a molecule containing a cyclobutane ring (51), cf. Diagram 5c.

The adduct (52) of cyclooctatetraene, and dimethyl acetylene dicarboxylate, first described by Reppe,[19] will act as a further dienophile. The product can be pyrolysed to yield dimethyl phthalate, and a molecule with a cyclobutane moiety, (53), cf. Diagram 5d.

These methods, and the photochemical reactions of the compounds obtained by them, are discussed in Section 2(b).

The second approach to the problem of the stereochemistry of the dimer of (1) is to examine the nuclear magnetic resonance spectra of the model compounds since chemical shifts and spin, spin couplings are dependent not only on the proximity to each other of the substituents, but on the asymmetry of the molecule as well.

A refinement of the n.m.r. technique is to take advantage of the fact that all carbon compounds contain about 1.1% of the C^{13} carbon isotope, which has a spin of $\frac{1}{2}$ and couples strongly to a directly attached proton, giving rise to a weak but observable doublet straddling the $C^{12}H$ peak. The $C^{13}H$ doublet members would be split by the $C^{12}H$, if any, on adjacent carbon atoms in the cyclobutane ring.

It should thus be possible to differentiate between <u>cis</u>-vicinal hydrogens and <u>trans</u>-vicinal hydrogens by the extent of the splitting of the $C^{13}H$ doublet, thereby obtaining direct information

on the stereochemistry of two possible ring isomers. If the $C^{13}H$ doublet were not split this would indicate the absence of vicinal $C^{12}H$ groups, and thus indicate a 1,3-positioning of the two methyl groups in the cyclobutane ring.

So far the technique only allows the 1,2 positions to be of differentiated from the 1,3 positions since the coupling constant for cis vicinal hydrogens is equivalent to the coupling constant for trans-vicinal hydrogens in a cyclobutane system with some degree of flexibility. It can be applied more fully to real dimers of the types discussed, due to the fact that the dimers are now asymmetric and rigid in configuration and it may now be possible to differentiate between cis-vicinal hydrogens' and trans-vicinal hydrogens' H,H couplings, and so distinguish between syn- and anti-isomers.

An examination of the n.m.r. spectra of model compounds containing dimethyl-substituted cyclobutane ring systems of known or suggested stereochemistry such as (10), (37), and the dimers (53) obtained on photocycloaddition of the pyrimidine nucleic acid base components, thymine (54,R = CH_3), and (55,R = H)[15] could resolve the question of the stereochemistry of the dimer of (1). The stereochemistry of the dimers (54), and (55) has been studied by the $C13_H$ satellite technique.[20]

The results obtained from this approach are discussed in the sub-section 2(f) on the stereochemistry of 2-methyl-1,4-naphthoquinone dimer.

SECTION 2

PHOTOCYCLOADDITION AND ELIMINATION REACTIONS

2(a) The Synthesis and Photochemistry of Cis-1,2-Dimethyl-Cyclohexa-3,5-Diene-1,2-Dicarboxylic Anhydride (56)

Various methods have been used in the synthesis of conjugated cyclohexadienes, including Diels-Alder reactions and in one case[2] the reduction of phthalic acid (57)[21] to cyclohexa-2,3-diene-1,2 dicarboxylic acid (58), followed by ring closure to the anhydride (41). These methods are represented in Diagram 6.

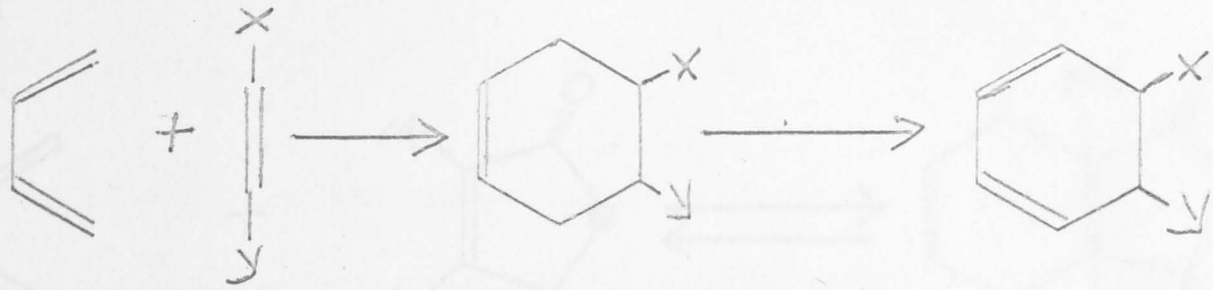
The method outlined in Diagram 6a was chosen on the precedence of Woodward[22] and Ziegler[23] who have described the sequence of reactions leading to the diene-anhydride (56), cf. Diagram 7.

The preparation of the olefin-anhydride (57) in 76% yield was reported by Ziegler, and 30% yield by Woodward. The conditions followed for the Diels-Alder reaction were essentially those described by Ziegler, but using an Aminco High-Pressure Assembly. The actual extraction and purification of the olefin-anhydride (57) was carried out according to the method of Woodward. The yield of (57) obtained was up to 40%. Bromination of (57) gave the dibromo compound (58) in high yield (95%).

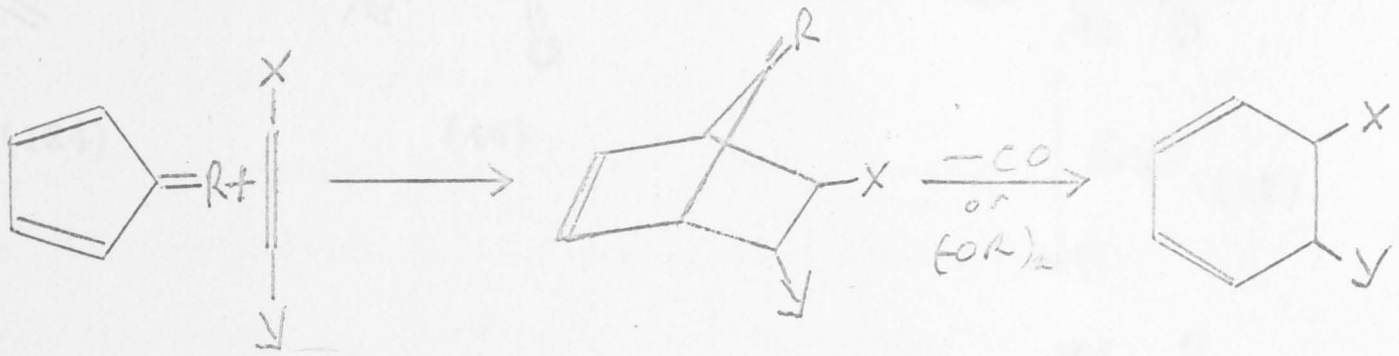
Treatment of (57) with s-collidine after the method of Ziegler gave low yields of the diene-anhydride (56). In the German Patent,[23] Ziegler claimed the synthesis of (56) in 70% yield by dehydrobromination of (58) with s-collidine. In an earlier report,[24]

DIAGRAM 6

(a)

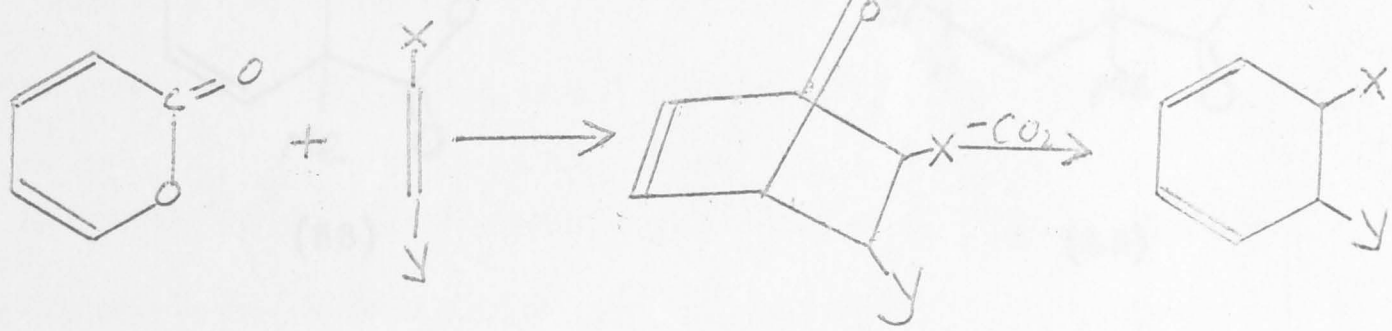


(b)

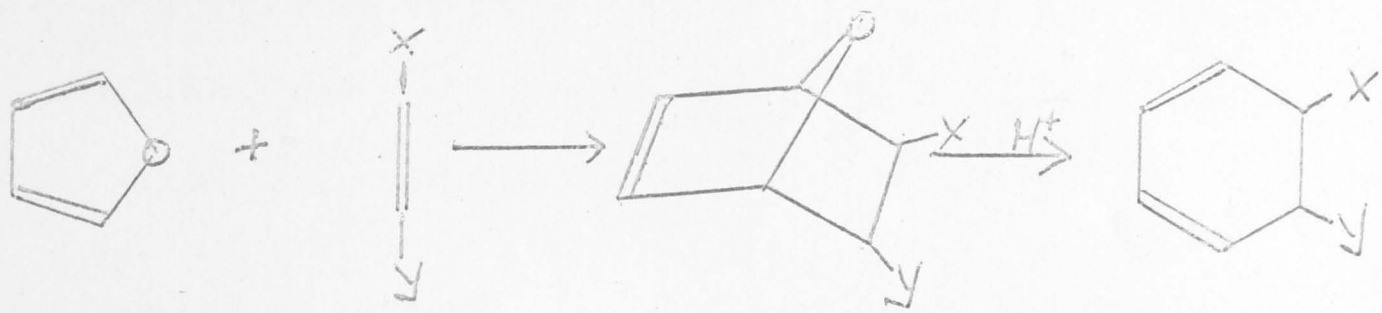


R = O = $(OR)_2$

(c)



(d)



(e) Reduction:

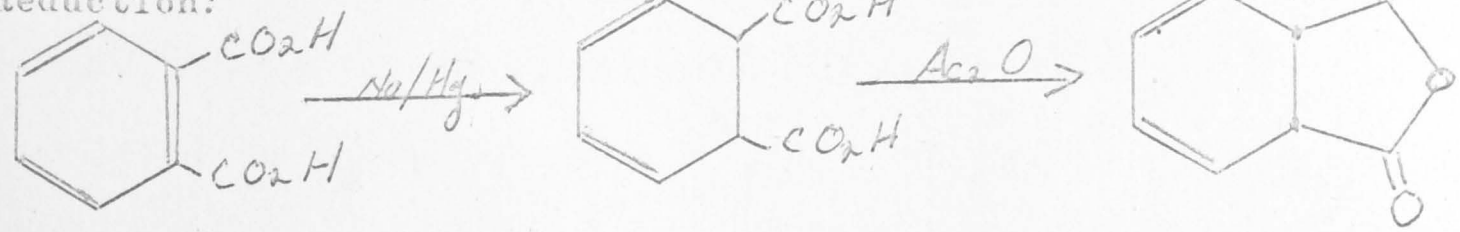
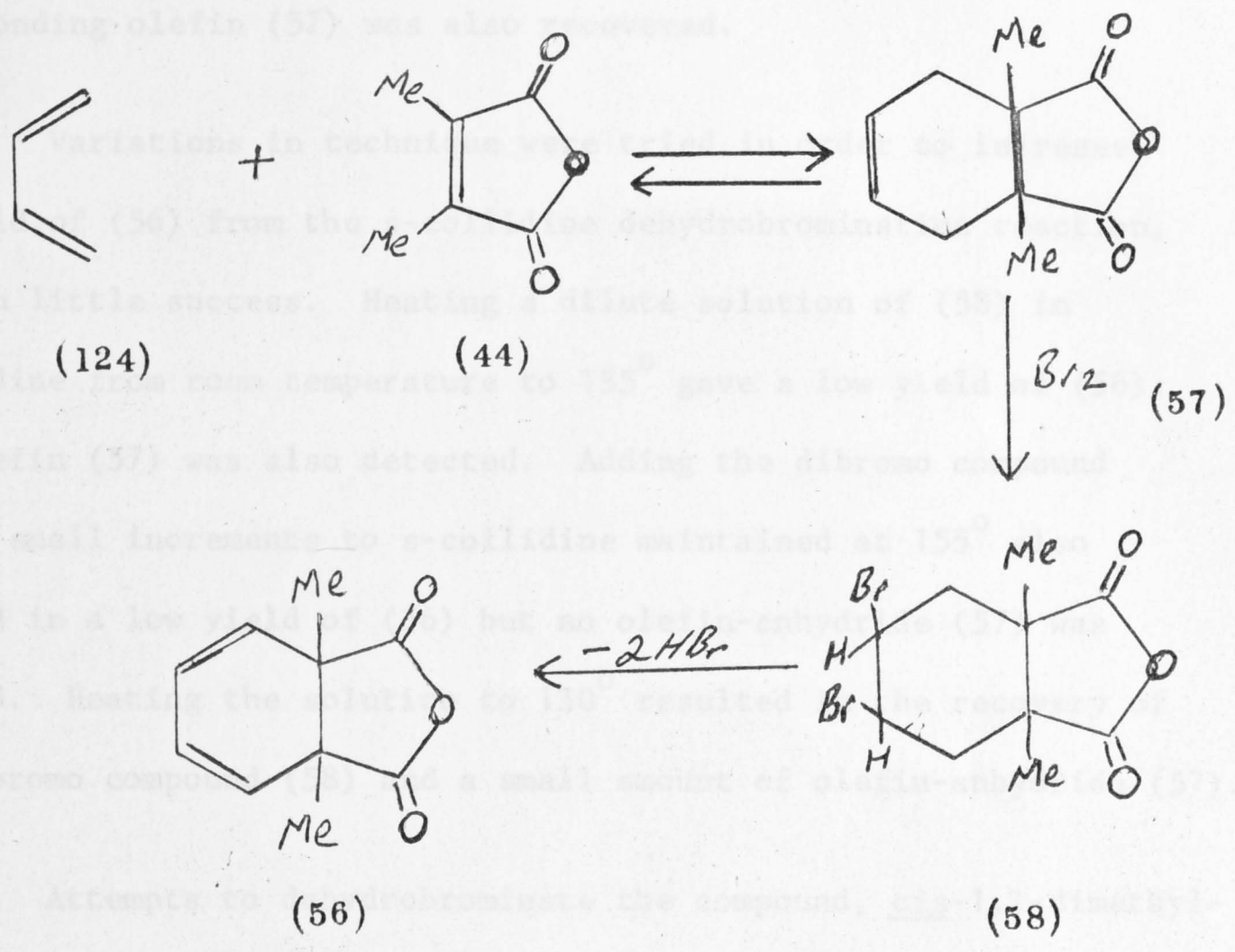


DIAGRAM 7



(124) (44) (56) (58)

Ziegler and co-workers obtained (56) in 10% yield only, by dehydrobromination with triethyl amine. A small amount of the corresponding olefin (57) was also recovered.

Variations in technique were tried in order to increase the yield of (56) from the s-collidine dehydrobromination reaction, but with little success. Heating a dilute solution of (58) in s-collidine from room temperature to 155° gave a low yield of (56). Some olefin (57) was also detected. Adding the dibromo compound (58) in small increments to s-collidine maintained at 155° also resulted in a low yield of (56) but no olefin-anhydride (57) was detected. Heating the solution to 130° resulted in the recovery of some dibromo compound (58) and a small amount of olefin-anhydride (57).

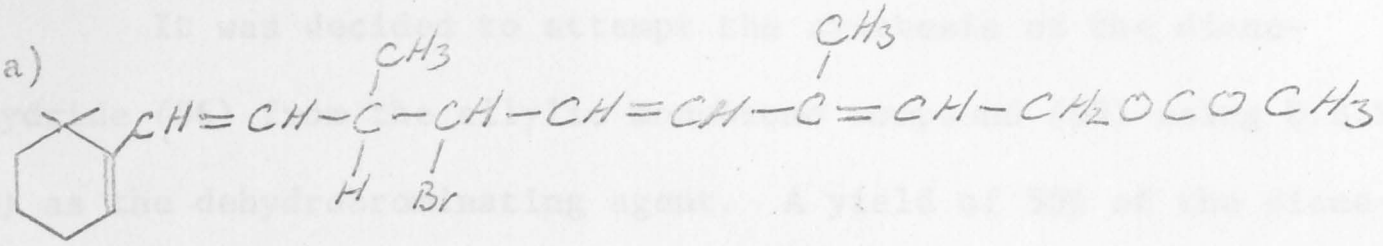
Attempts to dehydrobrominate the compound, cis-1,2-dimethyl-3-bromo-cyclohex-4-ene-1,2-dicarboxylic anhydride (59) to give (56) by setting aside a solution of the compound in s-collidine at room temperature for 2 or 3 days were unsuccessful, as were attempts to dehydrobrominate (59) in s-collidine at 155°.

Öediger and co-workers,[25a] in 1966, described the preparation of the compound 1,5-diaza-bicyclo (4,3,0) non-5-ene (D.B.N.) (60). D.B.N. (60) according to their report had the ability to dehydrobrominate, under mild conditions a variety of compounds. A selection of these dehydrobrominations is shown in Diagram 8.

Vogel and co-workers[25b] have reported obtaining oxepin (61) in good yield from 1,2-epoxy, 4,5 dibromo cyclohexane (62) with the use of D.B.N. (60).

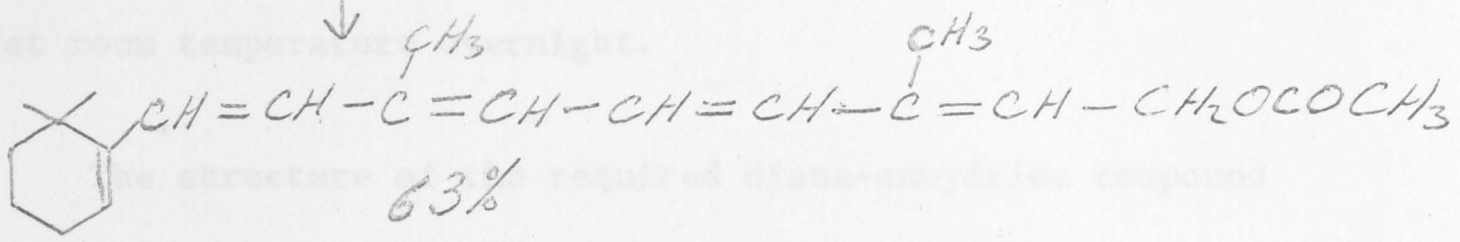
DIAGRAM 8.

(a)



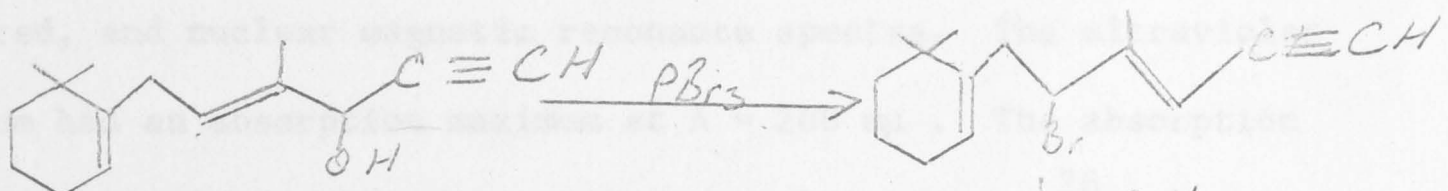
D.B.N.

(b)

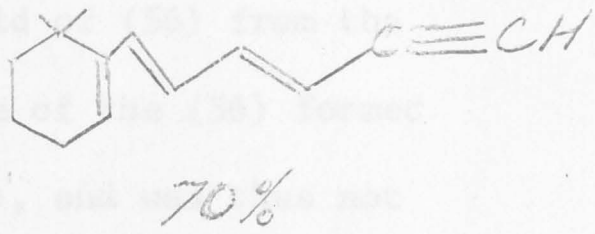


63%

(c)

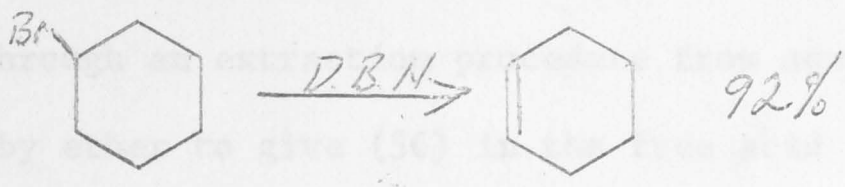


D.B.N



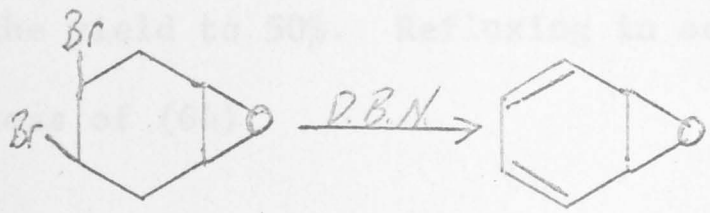
70%

(d)



92%

(e)



(62) (61)

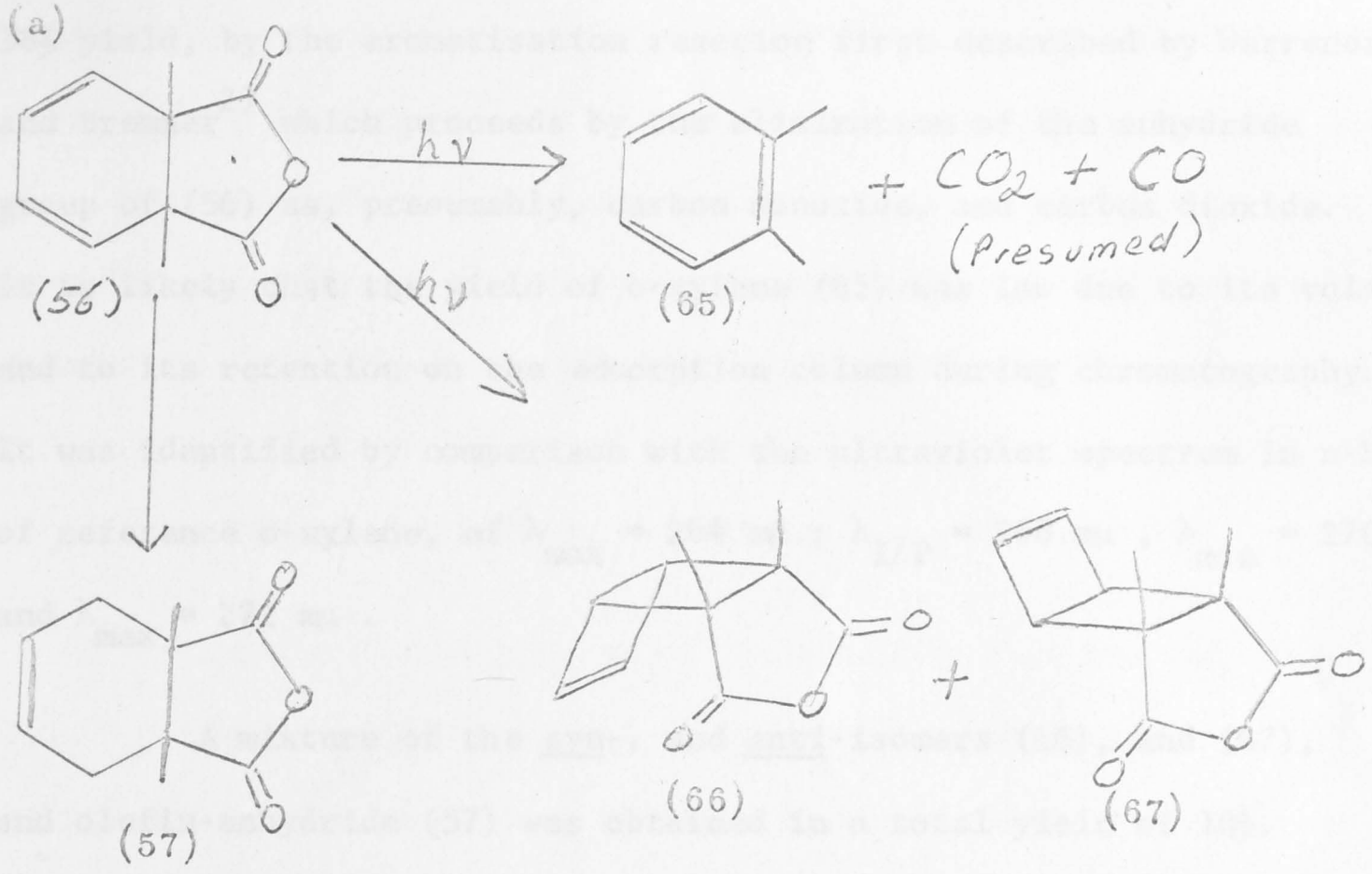
It was decided to attempt the synthesis of the diene-anhydride (56) from the allylic monobromo compound (59) using D.B.N. (60) as the dehydrobrominating agent. A yield of 50% of the diene-anhydride (56) was obtained under the very mild conditions of setting aside at room temperature overnight.

The structure of the required diene-anhydride compound (56) was supported by analysis ($C_{10}H_{10}O_3$), and also by its ultraviolet, infra-red, and nuclear magnetic resonance spectra. The ultraviolet spectrum had an absorption maximum at λ = 260 mμ . The absorption maximum for cyclohexa-1,3-diene (63) is at λ = 256 mμ .[26]

It was further thought that the yield of (56) from the reaction could have been higher, and that some of the (56) formed was bound as a salt of the D.B.N. reagent (60), and was thus not extractable by the technique used. Accordingly, the reaction mixture was put through an extraction procedure from aqueous mineral acid solution by ether to give (56) in the free acid form in quantitative yield. The conversion of the free acid (64) to the diene anhydride (56) by refluxing in benzene with toluene sulphonic acid as catalyst, reduced the yield to 50%. Refluxing in acetyl chloride resulted in greater loss of (64).

Ultraviolet-light irradiation of (56) in ether, under an inert atmosphere resulted in conversion to o-xylene (65), olefin-anhydride (57) and the isomeric <u>syn</u>-, and <u>anti</u>-5,6-dimethyl-bicyclo (2,2,0) cyclohexene-5,6-dicarboxylic anhydrides (66), and (67), cf. Diagram 9a.

DIAGRAM 9



The main reaction was the formation of o-xylene (65) in 38% yield, by the aromatisation reaction first described by Warrener, and Bremner[27] which proceeds by the elimination of the anhydride group of (56) as, presumably, carbon monoxide, and carbon dioxide. It is likely that the yield of o-xylene (65) was low due to its volatility, and to its retention on the adsorption column during chromatography. It was identified by comparison with the ultraviolet spectrum in n-hexane of reference o-xylene, of λ_{max} = 264 mμ ; $\lambda_{I/P}$ = 268 mμ , λ_{min} = 270 mμ , and λ_{max} = 272 mμ .

A mixture of the syn-, and anti-isomers (66), and (67), and olefin-anhydride (57) was obtained in a total yield of 10%. Inspection of the n.m.r. spectrum of the mixture gave an approximate ratio of olefin-anhydride (57), and the valence isomers, of 8:10:7 which was consistent with one of the two valence isomers being preferentially formed in the irradiation. An analysis of a sublimate of the mixture gave: Found C, 66.6; H, 5.8% which was of the order calculated C, 67.4; H, 5.7% for the valence isomers. It was not possible to fully resolve the mixture by column chromatography on silica gel. A solvent system of benzene/n-hexane (1:3 by volume) was used. Thin layer chromatography also, did not fully resolve the mixture which developed as an oval-shaped spot in benzene on silica gel. An exploratory attempt to separate the mixture by vapour phase chromatography also was not successful. Using Carbowax as the stationary phase and with a column temperature of 135° the mixture was eluted as two overlapping fractions. The explanation for the presence of only

two peaks was that one was due to the olefin-anhydride (57) and the other was due to the diene-anhydride (56) formed by thermal reversion, at the column temperature, of the valence isomers. This was confirmed in a separate experiment by heating the mixture at 200° for 10 minutes. Under these conditions the valence isomers (66), and (67) were thermally reverted to (56), which was identified by n.m.r. spectroscopy. This is consistent with the assigned structure. The olefin-anhydride remained unchanged under these conditions.

Because of the problem of isolating each of the two bicyclo (2,2,0) hexene isomers (66), and (67), and also the problem of assigning definite structures to them, it was decided to attempt to synthesise the syn-isomer by a separate procedure. Pettit, and co-workers[17] have reported the cycloaddition of dimethyl maleate (48) to cyclobut-1,3-diene (46). Repeating this experiment using dimethyl maleic anhydride (44) in place of the ester was considered as a possible means of making the syn-valence isomer, cf. Diagram 9b.

An attempt to prepare cyclobut-1,3-diene iron tricarbonyl (47) was made according to the method, briefly described by Pettit and co-workers.[28] A viscous, yellow oil was obtained which gave one signal τ = 6.18 (singlet) in its n.m.r. spectrum, and had carbonyl absorptions at ν_{max}: 2100 cm^{-1}, and ν_{max}: 1980 cm^{-1} in its infra-red spectrum. The compound (47) was described by Pettit as being pale yellow crystals, melting point 26°, with an n.m.r. spectrum of τ = 6.09 (singlet), and with carbonyl absorptions in the infra-red

spectrum at ν_{max}: 2055 cm^{-1} and ν_{max}: 1985 cm^{-1}. Although the product obtained was oil, and not a solid, it was considered on its spectral characteristics to be slightly impure cyclobuta-1,3-diene iron tricarbonyl compound (47). Unfortunately, attempts to repeat Pettit and co-workers' work and react this compound (47) with dimethyl maleate (48),[17] or with benzoquinone[29] met with no success. In each case, unchanged dimethyl maleate, or unchanged benzoquinone was recovered. Attempted correspondence with Pettit was equally unsuccessful.

Other means of introducing a cyclobutane system into a molecule were developed. These methods are described in Section 2(b), together with the photochemical behaviour of the compounds so derived.

2(b) Photocycloaddition and Elimination Reactions

It has been reported by Fonken[30] that the valence isomer (68), formed by irradiation of cyclooctatetraene (69), on further irradiation fragmented to form benzene (70) and acetylene (71), cf. Diagram 10a. Lemal and Shim[31] have described the photolysis of bicyclo (4,2,0) octa-2,4-diene (72) to give (70), and ethylene (73), cf. Diagram 10b.

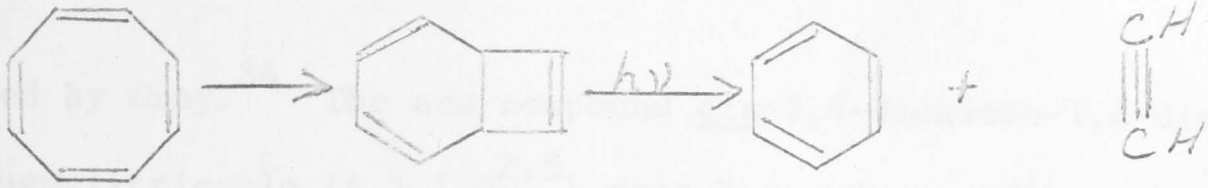
Warrener and Bremner's work,[27] and the work of Prinzbach and co-workers[32] on the photoaromatisation reaction of the compound 1,4,5,6-tetraphenyl-bicyclo (2,2,1) hept-5-ene-7-one-cis 2,3 dicarboxylic anhydride (74) was extended by Bremner[15] to the general case shown in Diagram 10c.

However, with substituted compounds with the potential of (68), one could expect, depending on the geometry of the molecule, to observe a competing internal photocycloaddition reaction which could give cage compounds of the homocubane type (75), cf. Diagram 10d. Such compounds (75) are of general interest in synthesis of cubanes.[33]

In order to prepare compounds with which to study possible competing photochemical reactions 2,5-dimethyl-3,4-diphenyl-cyclopenta-3,4-dienone dimer (76) was chosen as a suitable, and easily obtainable compound with which to work. It was prepared according to the method

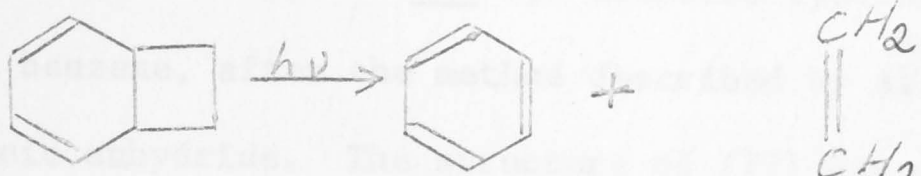
DIAGRAM 10

(a)



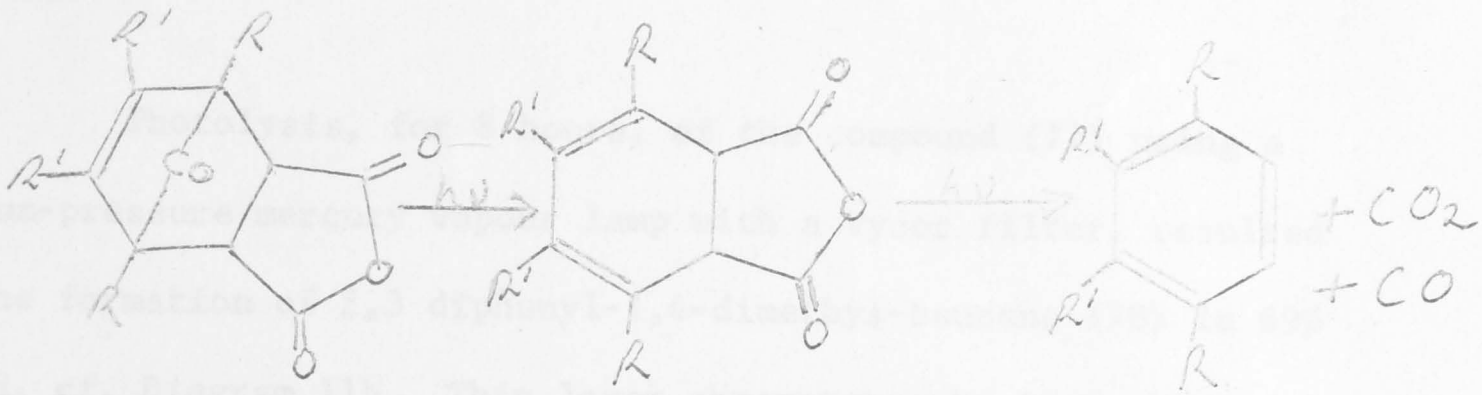
(69) (68) (70) (71)

(b)



(72) (70) (73)

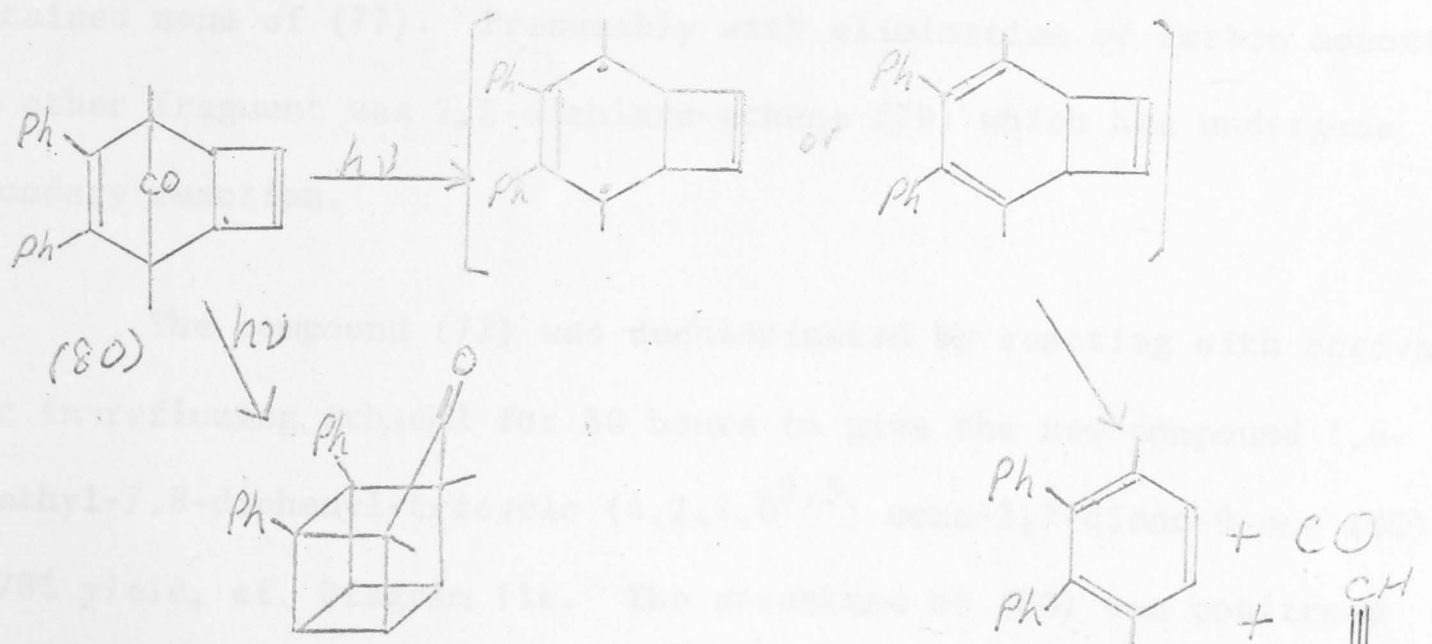
(c)



R' = Ph,
R = Ph = Me.

(74)

(d)



(80) (75) (78) (71)

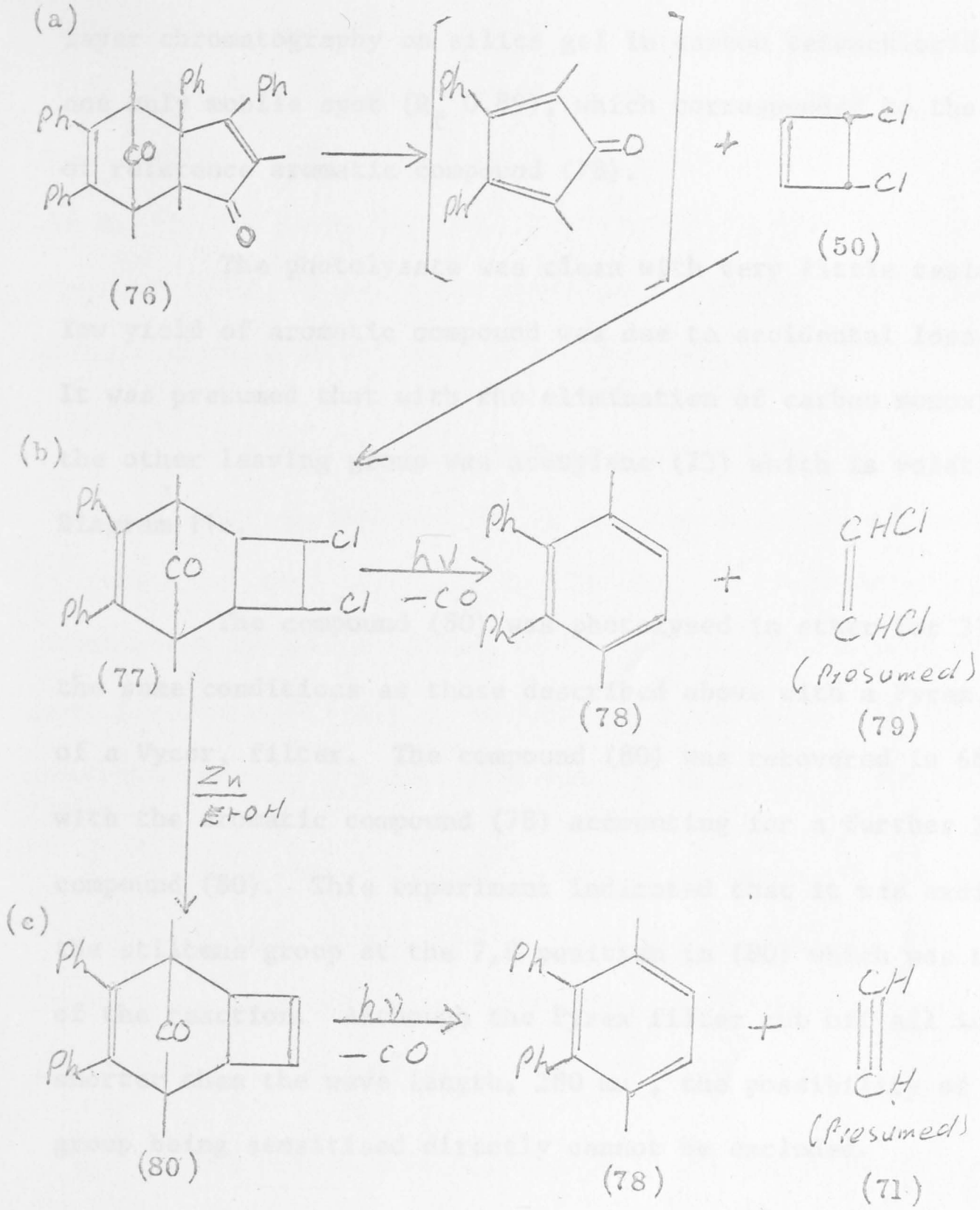
described by Gray.[34] The new compound cis-3,4-dichloro-1,6-dimethyl-7,8-diphenyl-tricyclo (4,2,1,$0^{2,5}$) nona-7-ene-9-one (77) was obtained in 52% yield by the reaction of (76), and cis-3,4-dichloro-cyclobut-1-ene (50) in refluxing benzene, after the method described by Allen, and Van Allen[35] for maleic anhydride. The structure of (77) was confirmed by analysis ($C_{23}H_{20}O\ Cl_2$), and by its n.m.r., and infra-red spectra.

Photolysis, for 8 hours, of the compound (77) using a medium-pressure mercury vapour lamp with a Vycor filter, resulted in the formation of 2,3 diphenyl-1,4-dimethyl-benzene (78) in 69% yield, cf. Diagram 11b. Thin layer chromatography in carbon tetrachloride on silica gel showed only one mobile spot R_f 0.86, as also did thin layer chromatography in n-hexane. The residue from the reaction gave a positive Beilstein-Marsh test for chlorine but contained none of (77). Presumably with elimination of carbon monoxide, the other fragment was 1,2-dichloro-ethene (79) which has undergone secondary reaction.

The compound (77) was dechlorinated by reacting with activated zinc in refluxing ethanol for 30 hours to give the new compound 1,6-dimethyl-7,8-diphenyl-tricyclo (4,2,1,$0^{2,5}$) nona-3,7-diene-9-one (80) in 78% yield, cf. Diagram 11c. The structure of (80) was confirmed by analysis ($C_{23}H_{20}O$), and by its n.m.r. and infra-red spectra.

Compound (80) was photolysed in ether for 8 hours, under the same conditions as those described for the chlorinated compound (77),

DIAGRAM 11


(a)
Ph
Ph
Ph
Ph
CO
O
(76)
Ph
Ph
O
+
Cl
Cl
(50)
(b)
Ph
Ph
CO
Cl
Cl
hν
−CO
(77)
Ph
Ph
(78)
+
CHCl
CHCl
(Presumed)
(79)
Zn
EtOH
(c)
Ph
Ph
CO
hν
−CO
(80)
Ph
Ph
(78)
+
CH
CH
(Presumed)
(71)

with the production of the aromatic compound in 56% yield. Thin layer chromatography on silica gel in carbon tetrachloride showed one only mobile spot (R_f 0.89), which corresponded to the R_f 0.89 of reference aromatic compound (78).

The photolysate was clean with very little residue. The low yield of aromatic compound was due to accidental loss in handling. It was presumed that with the elimination of carbon monoxide from (80) the other leaving group was acetylene (73) which is volatile, cf. Diagram 11c.

The compound (80) was photolysed in ether for 31 hours under the same conditions as those described above with a Pyrex, instead of a Vycor, filter. The compound (80) was recovered in 68% yield, with the aromatic compound (78) accounting for a further 28% of starting compound (80). This experiment indicated that it was excitation of the stilbene group at the 7,8 position in (80) which was the initiator of the reaction. Although the Pyrex filter cut off all irradiation shorter than the wave length, 280 mμ , the possibility of the carbonyl group being sensitised directly cannot be excluded.

Compound (80) was again photolysed, this time in acetone for 2 hours using a high-pressure mercury lamp with a Vycor filter. Examination of the photolysate by thin layer chromatography in carbon tetrachloride on silica gel showed a single mobile spot of R_f 0.8 corresponding to that of authentic aromatic compound (78) R_f 0.8.

Examination by thin layer on silica gel in n-hexane showed two mobile spots. One at R_f 0.4 corresponded to that of authentic diphenylacetylene (81). This showed a characteristic orange-red colouration after treatment with 10% ceric sulphate spray followed by heating. The other spot was at R_f 0.25 and corresponded to that of authentic aromatic compound (78). These latter spots gave a characteristic mauve colouration after treatment with 10% ceric sulphate spray followed by heating.

This mixture of diphenylacetylene (81) and the aromatic compound (78) was obtained in 37% w/w yield, by column chromatography on silica gel with carbon tetrachloride. An ultraviolet spectroscopic examination in dilute ethanol of the mixture showed part of an absorption spectrum characteristic of authentic diphenylacetylene (81) with absorptions at λ_{max} = 280, 288, and 297 mμ , λ_{min} = 286 and 293 mμ .

On a semi-quantitative basis, by inspection of the intensity of the thin layer spots, and by inspection of the relative ultraviolet absorptions of the mixture, there appeared to be about equal amounts present of the two compounds (81), and (78).

The presence of o-xylene (65) was not strictly proven except that, after elution from the column of the mixture of the above two compounds, an n.m.r. examination of some further carbon tetrachloride eluant, after careful evaporation of the solvent gave a spectrum similar to that of authentic o-xylene of τ = 2.73 (singlet with broadening at the base), and τ = 7.79 (singlet, methyl H).

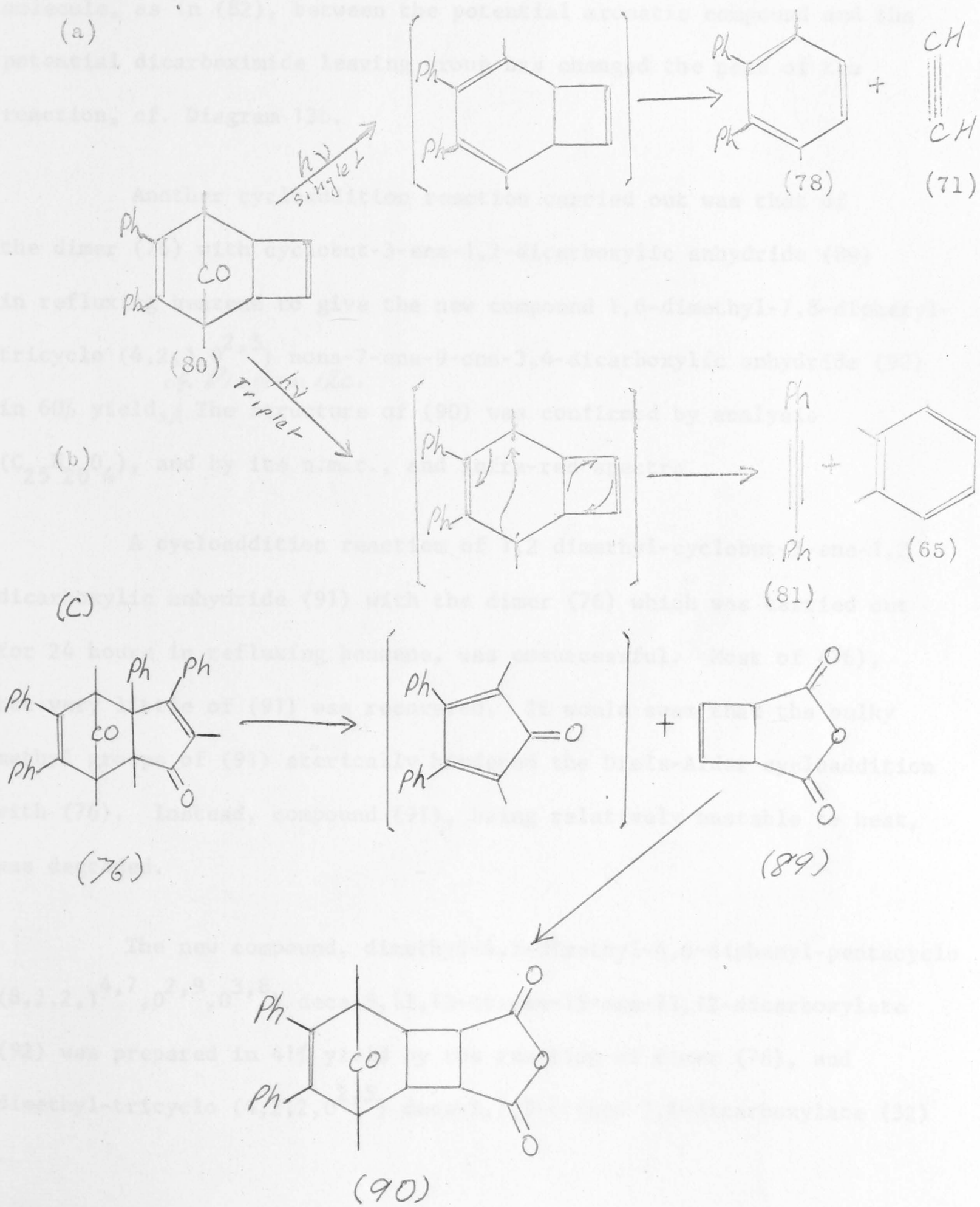
It appears that with acetone as a sensitising solvent, two photocycloelimination processes are competing. One an acetone-sensitised triplet reaction leading to diphenyl acetylene (81), and o-xylene (65), and the other a singlet reaction leading to the aromatic compound (78), and acetylene (71). These reactions are shown in Diagram 12. The presence of any cage structure formed by intra-molecular cycloaddition of (80), under the reaction conditions described was not detected.

The new compound, N-benzyl-1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one-3,4 dicarboximide (82) was prepared in 68% yield from the reaction of cyclopentadienone dimer (76), and N-benzyl-cyclobut-3-ene-1,2-dicarboximide (83) in refluxing benzene. The structure of (82) was confirmed by analysis ($C_{32}H_{27}O_3N$), and also by its n.m.r., and infra-red spectra.

Photolysis for $6\frac{1}{2}$ hours of (82) in acetone, using a high-pressure lamp with a Vycor filter gave the aromatic compound (78) in 94% yield, after column chromatography of the photolysate.

Further development of the column yielded N-benzyl-maleimide (84) contaminated by acetone photolytic products. Identification of (84) was by the infra-red spectrum having a strong main band, at ν_{max} 1700 cm^{-1}, similar to that of authentic N-benzyl-maleimide (84). It was further identified by thin layer on silica gel in ether/hexane (1:1 by volume) when the eluted imide had an R_f 0.5 corresponding to that of authentic N-benzyl-maleimide (84). Bremner[15] has photolysed

DIAGRAM 12



the compound (85) to give the compounds (86), (87), and (88), cf. Diagram 13a. He did not obtain any tetraphenylbenzenes nor detect any N-benzyl maleimide. The presence of a cyclobutane ring in the molecule, as in (82), between the potential aromatic compound and the potential dicarboximide leaving group has changed the path of the reaction, cf. Diagram 13b.

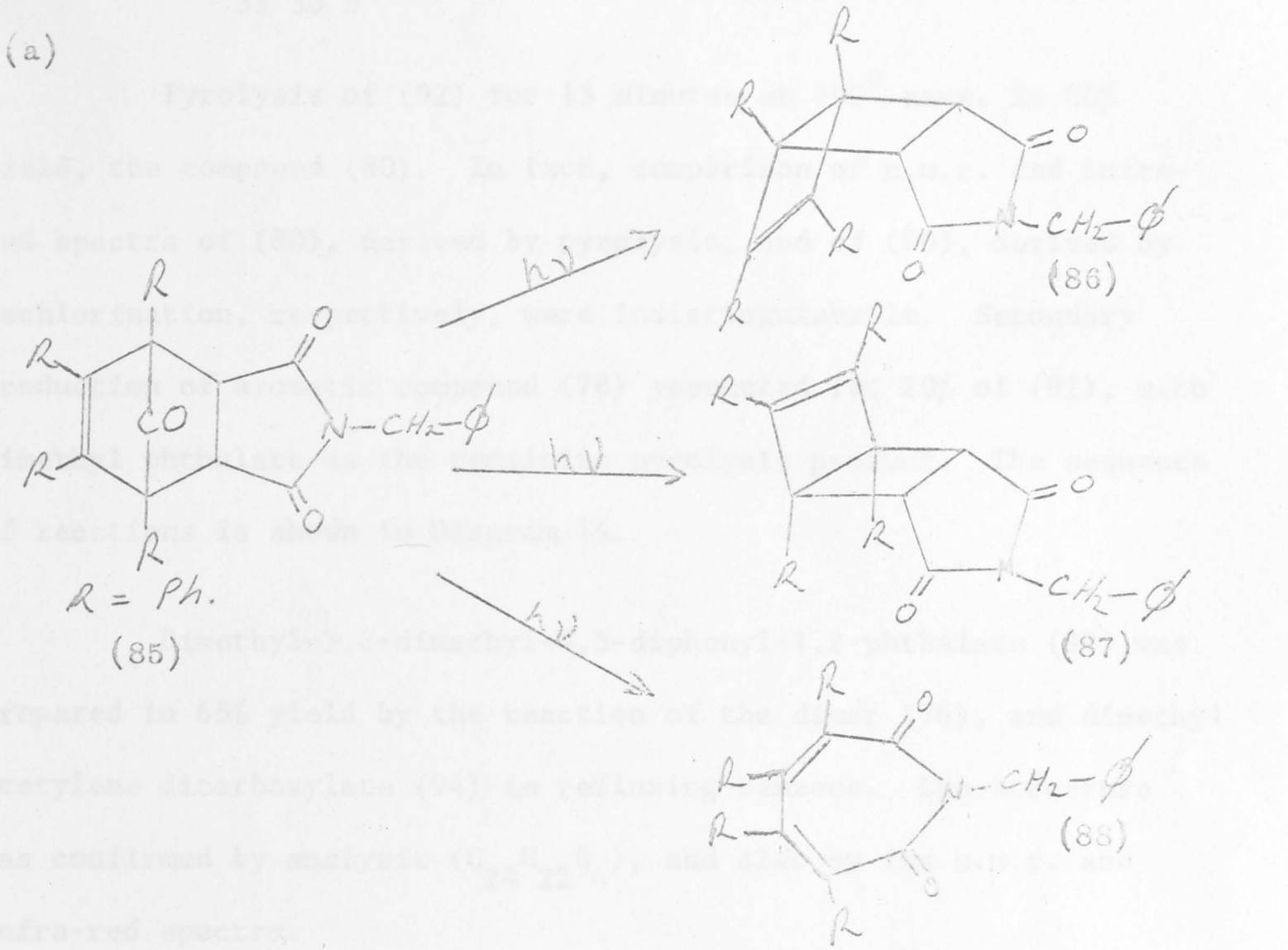
Another cycloaddition reaction carried out was that of the dimer (76) with cyclobut-3-ene-1,2-dicarboxylic anhydride (89) in refluxing benzene to give the new compound 1,6-dimethyl-7,8-diphenyl-tricyclo $(4,2,1,0^{2,5})$ nona-7-ene-9-one-3,4-dicarboxylic anhydride (90) in 60% yield, cf. Diagram 12c. The structure of (90) was confirmed by analysis ($C_{25}H_{20}O_4$), and by its n.m.r., and infra-red spectra.

A cycloaddition reaction of 1,2 dimethyl-cyclobut-3-ene-1,2 dicarboxylic anhydride (91) with the dimer (76) which was carried out for 24 hours in refluxing benzene, was unsuccessful. Most of (76), but very little of (91) was recovered. It would seem that the bulky methyl groups of (91) sterically hindered the Diels-Alder cycloaddition with (76). Instead, compound (91), being relatively unstable to heat, was degraded.

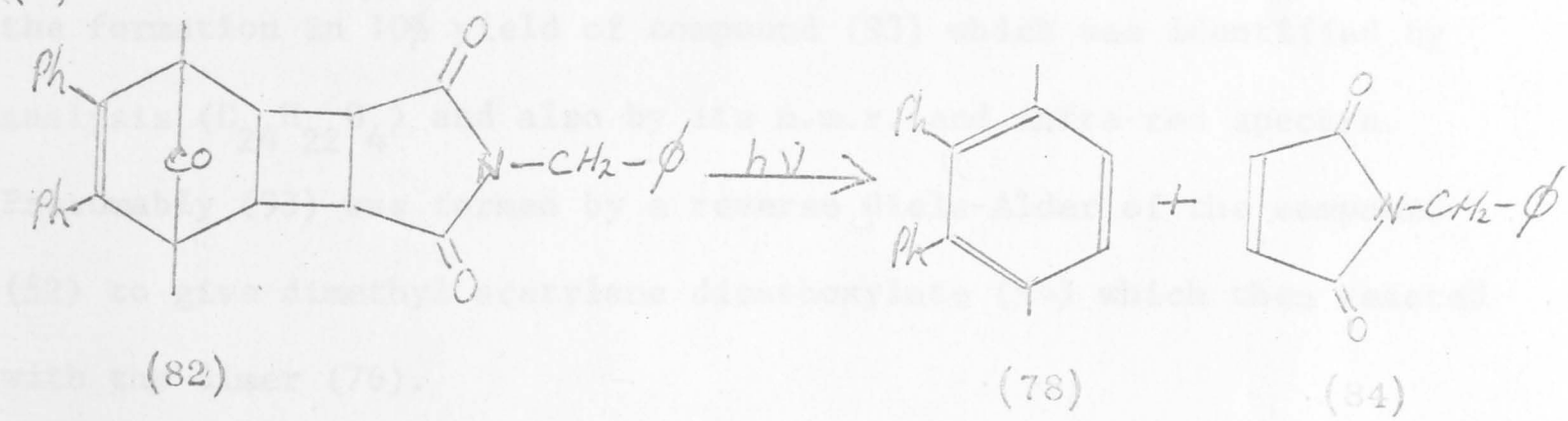
The new compound, dimethyl-4,5-dimethyl-4,6-diphenyl-pentacyclo $(8,2,2,1^{4,7},0^{2,9},0^{3,8})$ deca-5,11,13-triene-15-one-11,12-dicarboxylate (92) was prepared in 41% yield by the reaction of dimer (76), and dimethyl-tricyclo $(4,2,2,0^{2,5})$ deca-3,7,9-triene 7,8-dicarboxylate (52)

DIAGRAM 13

(a)



(b)



in gently refluxing chloroform. The structure of (92) was confirmed by analysis ($C_{33}H_{30}O_5$) and by its n.m.r., and infra-red spectra.

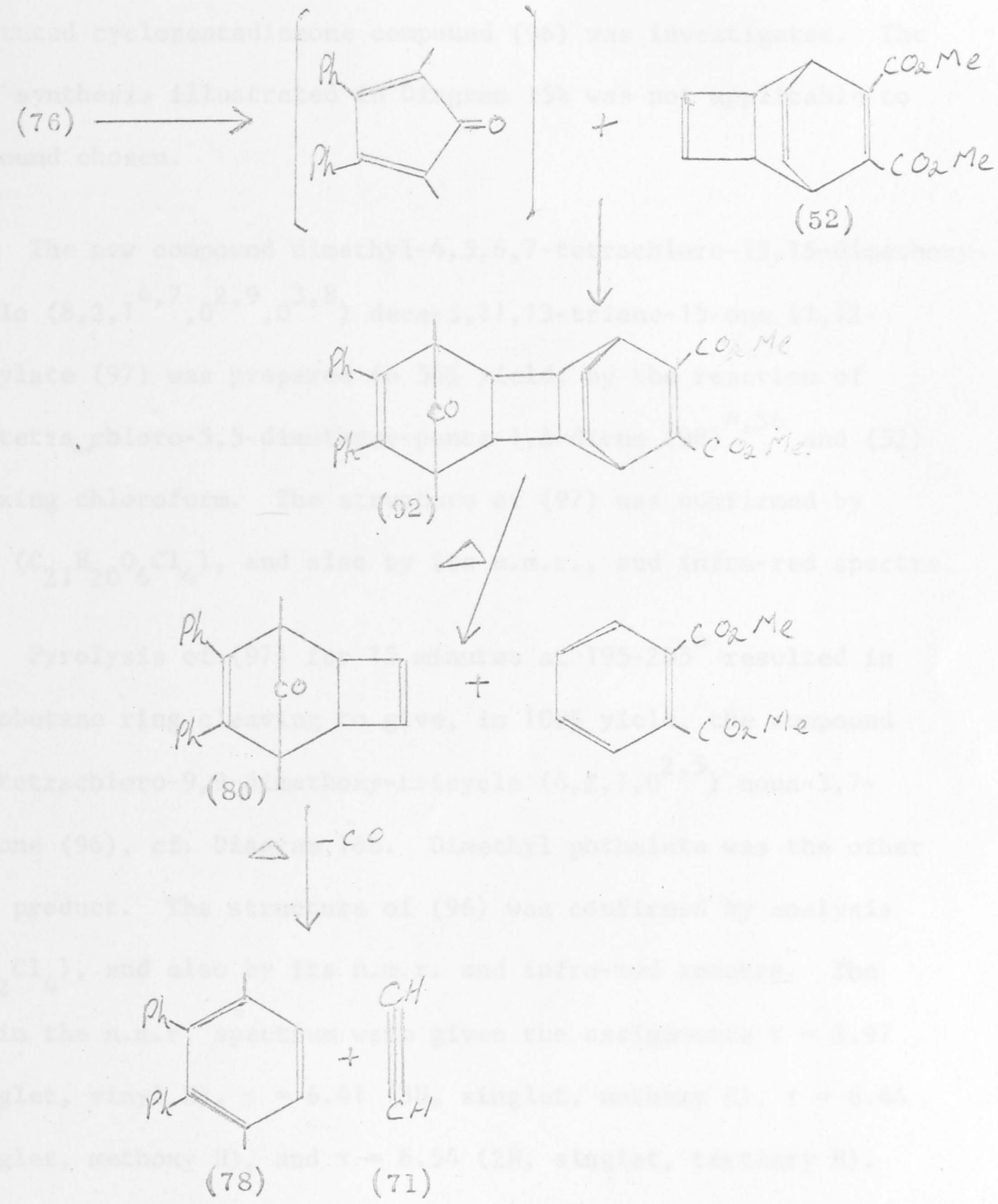
Pyrolysis of (92) for 15 minutes at 190° gave, in 80% yield, the compound (80). In fact, comparison of n.m.r. and infra-red spectra of (80), derived by pyrolysis, and of (80), derived by dechlorination, respectively, were indistinguishable. Secondary production of aromatic compound (78) accounted for 20% of (92), with dimethyl phthalate as the remaining pyrolysis product. The sequence of reactions is shown in Diagram 14.

Dimethyl-3,6-dimethyl-4,5-diphenyl-1,2-phthalate (93) was prepared in 65% yield by the reaction of the dimer (76), and dimethyl acetylene dicarboxylate (94) in refluxing benzene. The structure was confirmed by analysis ($C_{24}H_{22}O_4$), and also by its n.m.r. and infra-red spectra.

An attempt to prepare the compound (92) by the reaction of dimer (76), and the compound (52) in refluxing benzene resulted in the formation in 10% yield of compound (93) which was identified by analysis ($C_{24}H_{22}O_4$) and also by its n.m.r. and infra-red spectra. Presumably (93) was formed by a reverse Diels-Alder of the compound (52) to give dimethyl acetylene dicarboxylate (94) which then reacted with the dimer (76).

In order to overcome carbonyl elimination in photolysis, and also to demonstrate the versatility of the approach used in the

DIAGRAM 14


(a)
(76)
Ph
Ph
=O
+
CO2Me
CO2Me
(52)
CO2Me
Ph
CO
Ph
CO2Me
(92)
(b)
Ph
CO
Ph
+
CO2Me
CO2Me
(80)
-CO
Ph
Ph
+
CH
CH
(78)
(71)

preparation of the compound (80) by pyrolysis of (92), the acetal of a substituted cyclopentadienone compound (96) was investigated. The route of synthesis illustrated in Diagram 15b was not applicable to the compound chosen.

The new compound dimethyl-4,5,6,7-tetrachloro-15,15-dimethoxy-pentacyclo ($8,2,1^{4,7},0^{2,9},0^{3,8}$) deca-5,11,13-triene-15-one 11,12-dicarboxylate (97) was prepared in 54% yield, by the reaction of 1,2,3,4-tetrachloro-5,5-dimethoxy-penta-1,3-diene (98)*,[36] and (52) in refluxing chloroform. The structure of (97) was confirmed by analysis ($C_{21}H_{20}O_6Cl_4$), and also by its n.m.r., and infra-red spectra.

Pyrolysis of (97) for 15 minutes at 195-205° resulted in the cyclobutane ring cleaving to give, in 100% yield, the compound 1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (96), cf. Diagram 16b. Dimethyl phthalate was the other cleavage product. The structure of (96) was confirmed by analysis ($C_{11}H_{10}O_2Cl_4$), and also by its n.m.r. and infra-red spectra. The signals in the n.m.r. spectrum were given the assignments τ = 3.97 (2H, singlet, vinyl H), τ = 6.41 (3H, singlet, methoxy H), τ = 6.44 (3H, singlet, methoxy H), and τ = 6.54 (2H, singlet, tertiary H). The methoxy groups being in different environments were split into two sharp peaks. The methine hydrogens showed signs of slight

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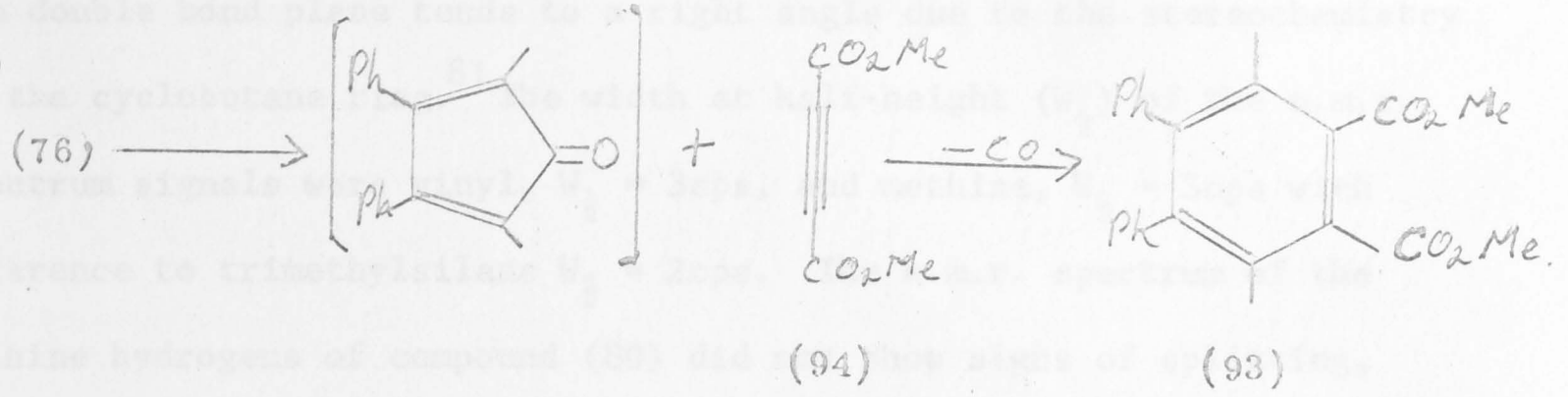
* Supplied by Dr. J.B. Bremner of this Department.

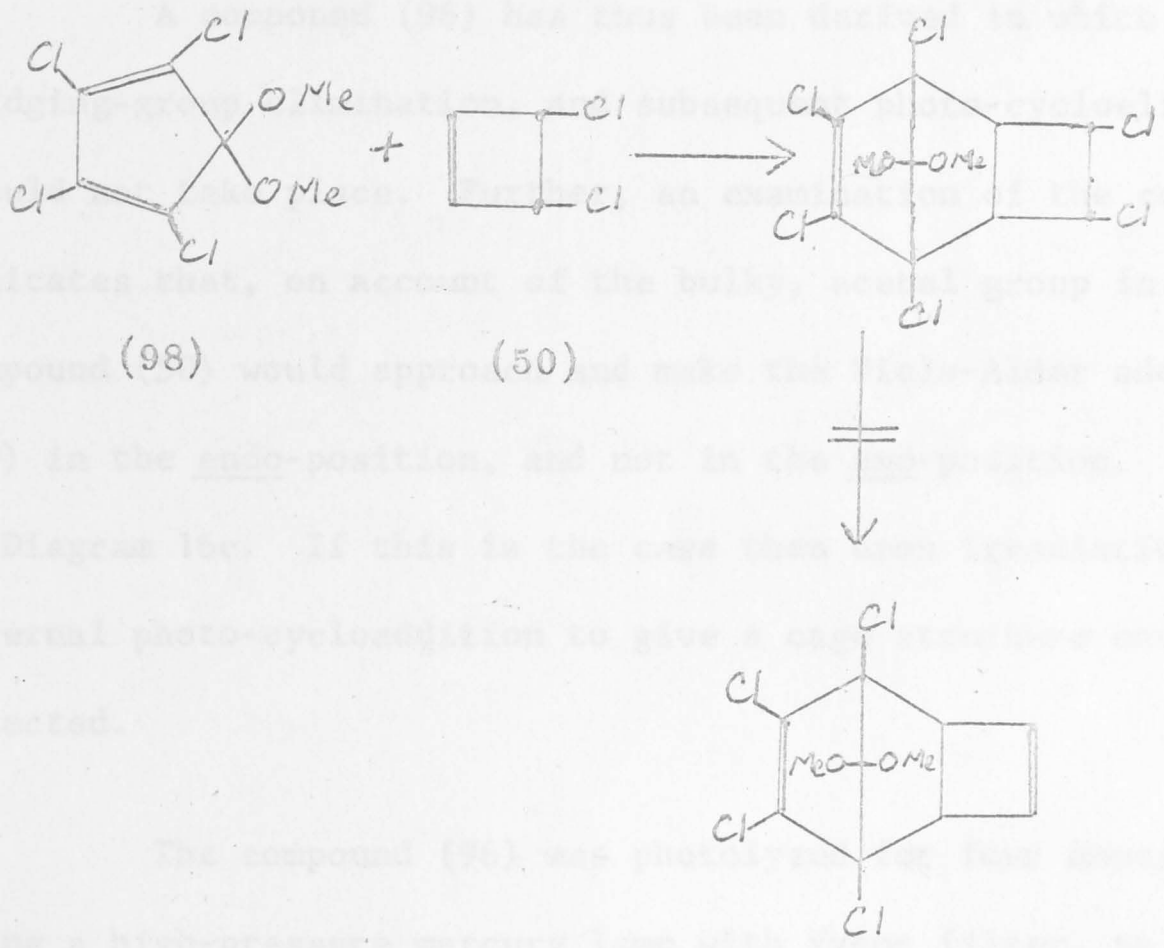
DIAGRAM 15

(a)



(94) (93)

(b)



(98) (50)

(96)

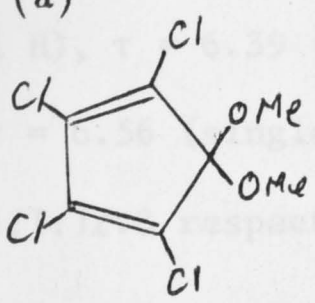
splittings consistent with the coupling of the methine hydrogens to the vinylic hydrogens as the angle between the methine hydrogens and the double bond plane tends to a right angle due to the stereochemistry of the cyclobutane ring.[81] The width at half-height ($W_{\frac{1}{2}}$) of the n.m.r. spectrum signals were vinyl, $W_{\frac{1}{2}}$ = 3cps, and methine, $W_{\frac{1}{2}}$ = 3cps with reference to trimethylsilane $W_{\frac{1}{2}}$ = 2cps. The n.m.r. spectrum of the methine hydrogens of compound (80) did not show signs of splitting, but had a methine, $W_{\frac{1}{2}}$ = 4cps with reference to trimethylsilane $W_{\frac{1}{2}}$ = 2cps.

A compound (96) has thus been derived in which carbonyl bridging-group elimination, and subsequent photo-cycloelimination should not take place. Further, an examination of the compound (97) indicates that, on account of the bulky, acetal group in (98), the compound (50) would approach and make the Diels-Alder adduct with (98) in the endo-position, and not in the exo-position. Illustrated in Diagram 16c. If this is the case then upon irradiation of (96) internal photo-cycloaddition to give a cage structure could be expected.

The compound (96) was photolysed for four hours in ether, using a high-pressure mercury lamp with Vycor filter, to give in 74% yield a colourless oil (99). This gave a single, mobile spot of R_f 0.52 on thin layer chromatography on silica gel in carbon tetrachloride. The signals in the n.m.r. spectrum of (99) were given the assignments τ = 4.03 (singlet, vinyl H), τ = 4.18 (singlet,

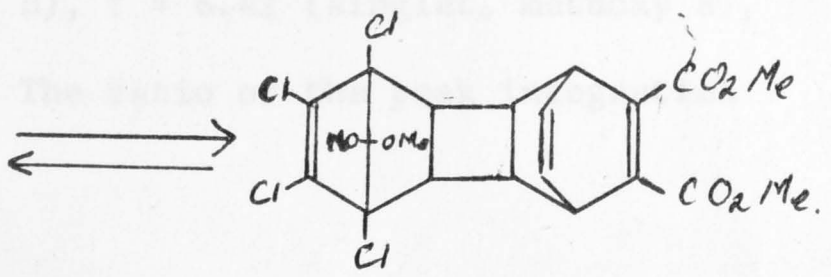
DIAGRAM 16

(a)



(98)

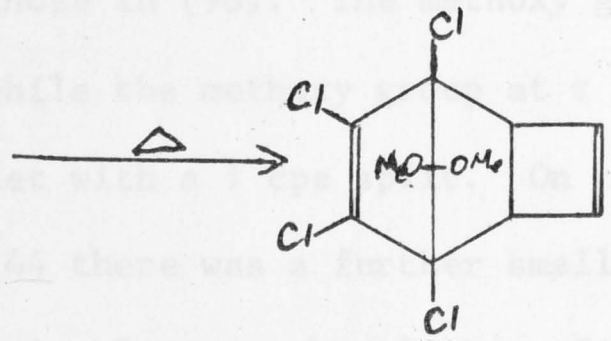
+ (52)



(97)

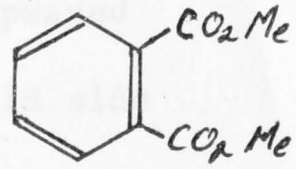
(b)

(97)



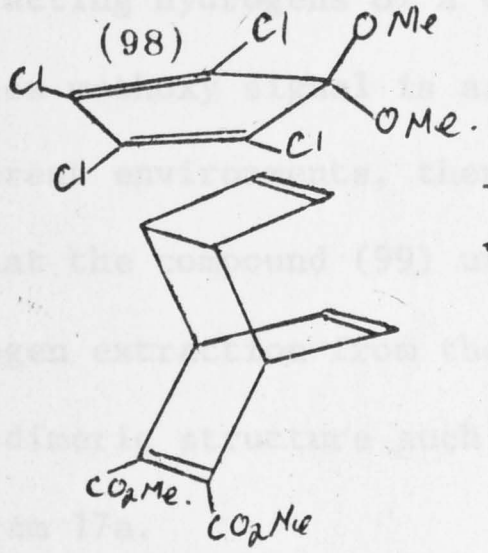
(96)

+

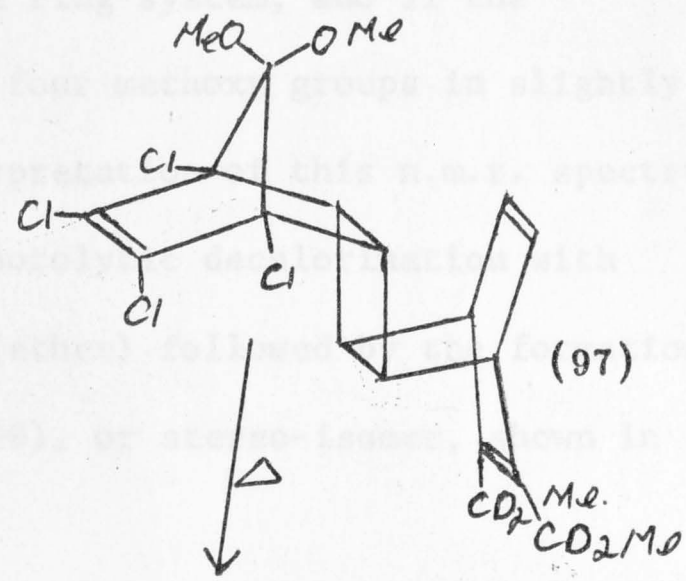


(c)

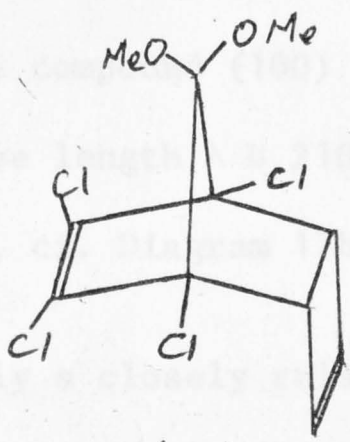
(98)



(52)

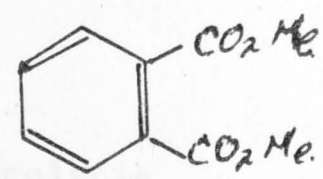


(97)



(96)

+



vinyl H), τ = 6.39 (singlet, methoxy H), τ = 6.42 (singlet, methoxy H), and τ = 6.56 (singlet, tertiary H). The ratio of the peak integration was 1:1:12.3 respectively.

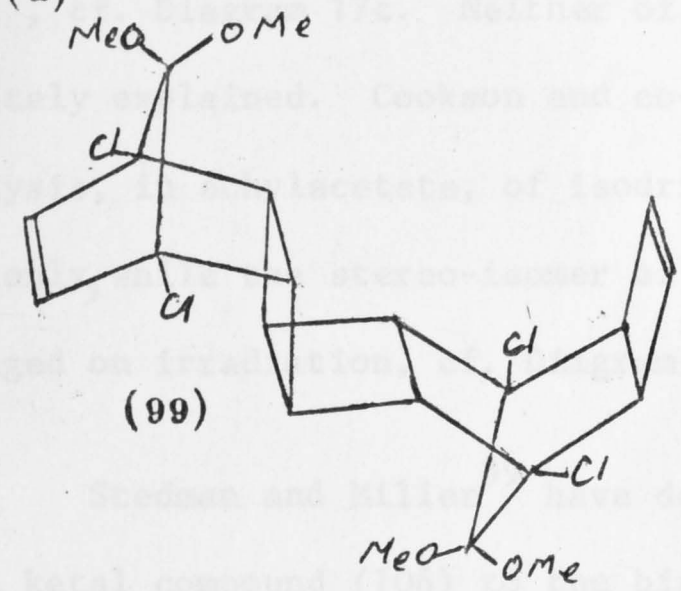
The methine hydrogens at τ = 6.56 showed the same signs of slight splitting as those in (96). The methoxy groups signals were more complex than those in (96). The methoxy group at τ = 6.39 appeared as a singlet, while the methoxy group at τ = 6.42 appeared to be split into a doublet with a 1 cps split. On the up-field side of this signal, at τ = 6.44 there was a further small sign of small splitting. The methoxy signals rose sharply out of a broad base signal of 30 cps. If this broad base signal is assigned to the interacting hydrogens of a cyclobutane ring system, and if the complex methoxy signal is assigned as four methoxy groups in slightly different environments, then one interpretation of this n.m.r. spectrum is that the compound (99) underwent photolytic dechlorination with hydrogen extraction from the solvent (ether) followed by the formation of a dimeric structure such as that (99), or stereo-isomer, shown in Diagram 17a.

Bremner[15] has photolysed the compound (100) in ether solution with ultraviolet light of wave length $\lambda \geqq 210$ mμ and obtained the mono-dechlorinated compound (101), cf. Diagram 17b.

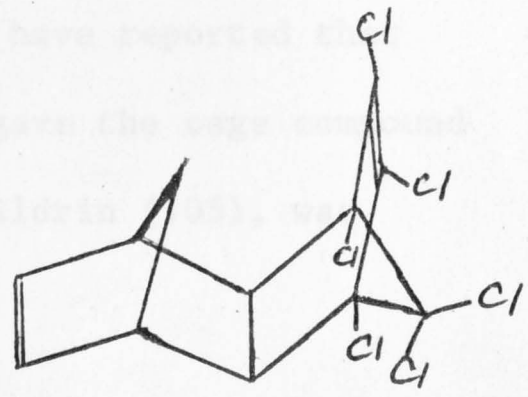
Henderson[37] reported recently a closely related photolytic dechlorination of isodrin epoxide (102) at wave lengths of less than

DIAGRAM 17

(a)

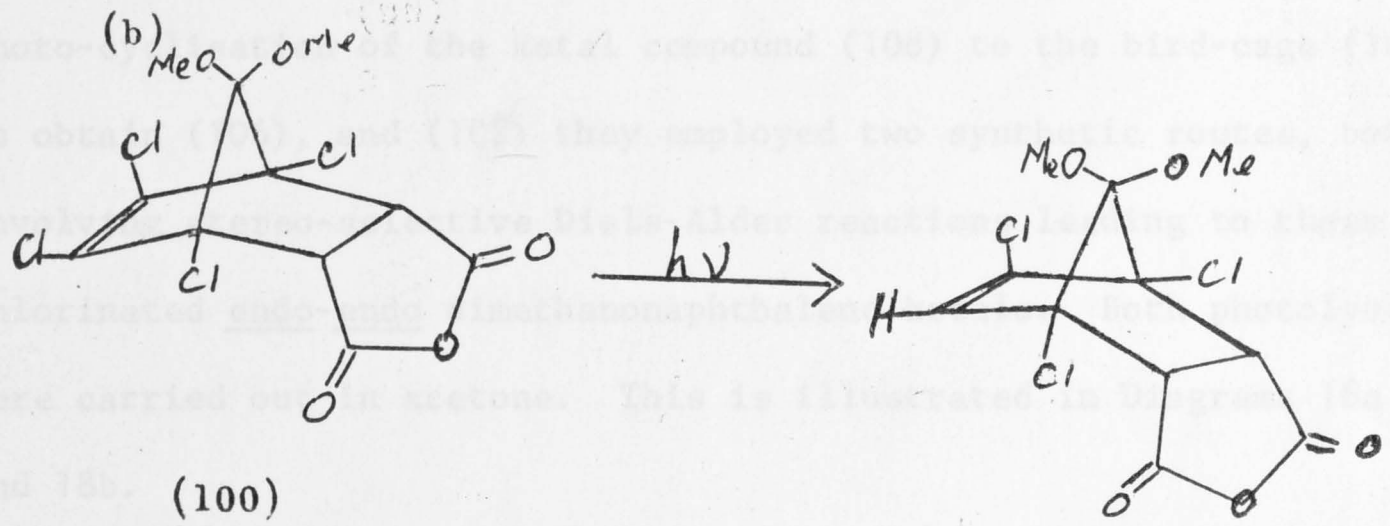


(99)



(105)*

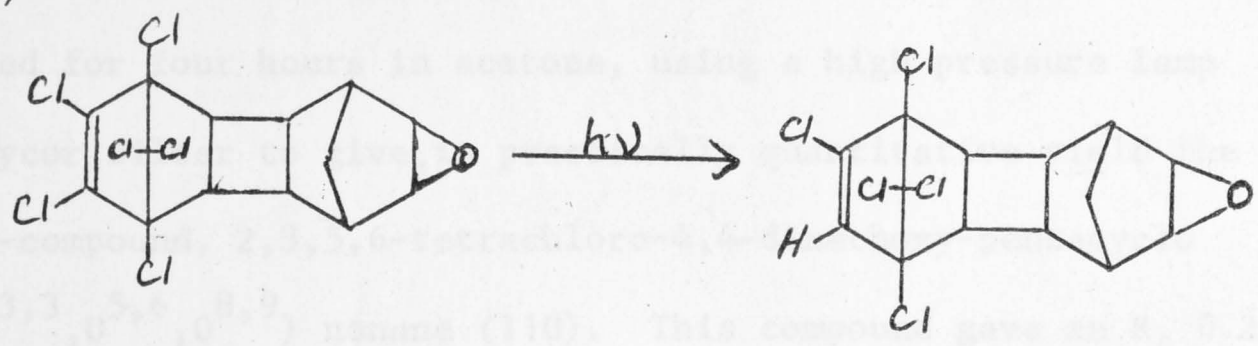
(b)



(100)

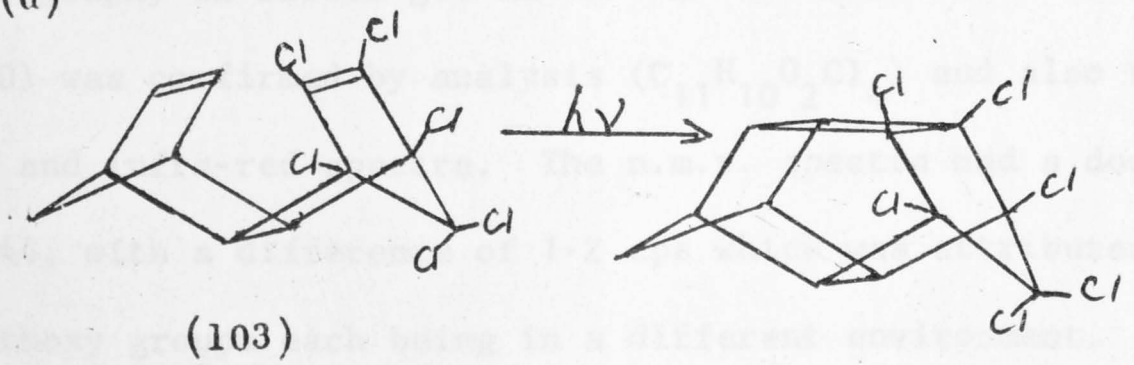
(101)

(c)



(102)

(d)



(103)

(104)

(105)*

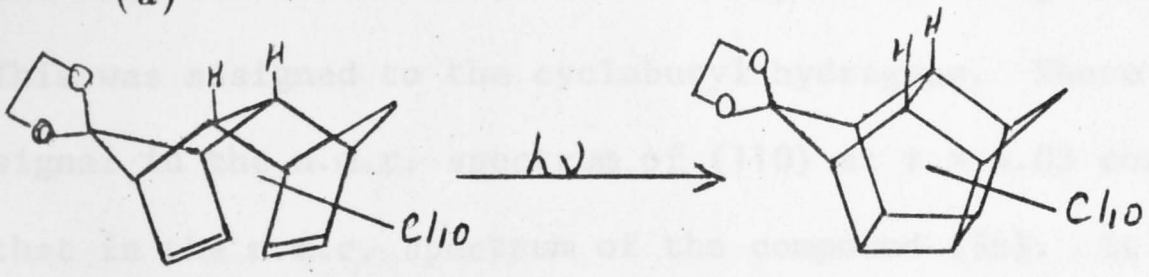
270 mμ , cf. Diagram 17c. Neither of these two results have been adequately explained. Cookson and co-workers[38] have reported that photolysis, in ethylacetate, of isodrin (103), gave the cage compound (104) only, while the stereo-isomer of isodrin, aldrin (105), was unchanged on irradiation, cf. Diagram 17d.

Stedman and Miller[39] have described the photo-cyclisation of the ketal compound (106) to the bird-cage (107), and also the photo-cyclisation of the ketal compound (108) to the bird-cage (109). To obtain (106), and (108) they employed two synthetic routes, both involving stereo-selective Diels-Alder reactions leading to these chlorinated endo-endo dimethanonaphthalene ketals. Both photolyses were carried out in acetone. This is illustrated in Diagrams 18a and 18b.

Accordingly the tetrachloro compound (96) was next photolysed for four hours in acetone, using a high pressure lamp with a Vycor filter to give, in practically quantitative yield the new cage-compound, 2,3,5,6-tetrachloro-4,4-dimethoxy-pentacyclo ($5,2,0,0^{3,3},0^{5,6},0^{8,9}$) nonane (110). This compound gave an R_f 0.24 quite distinct from that (R_f 0.8) of authentic (96) on thin layer chromatography on silica gel in carbon tetrachloride. The structure of (110) was confirmed by analysis ($C_{11}H_{10}O_2Cl_4$) and also by its n.m.r. and infra-red spectra. The n.m.r. spectra had a doublet at τ = 6.44, with a difference of 1-2 cps which was attributed to the two methoxy groups each being in a different environment. Around

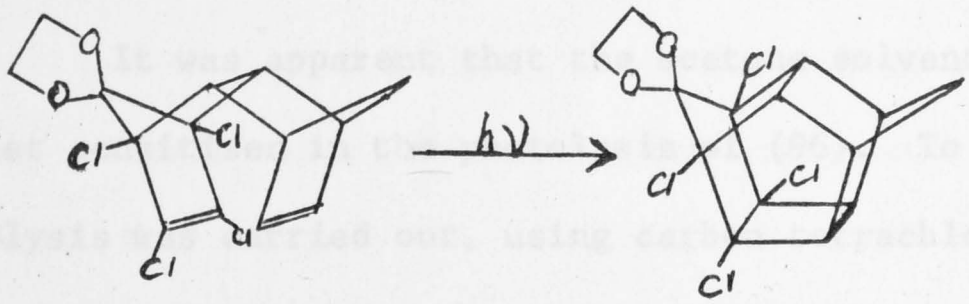
DIAGRAM 18

(a)



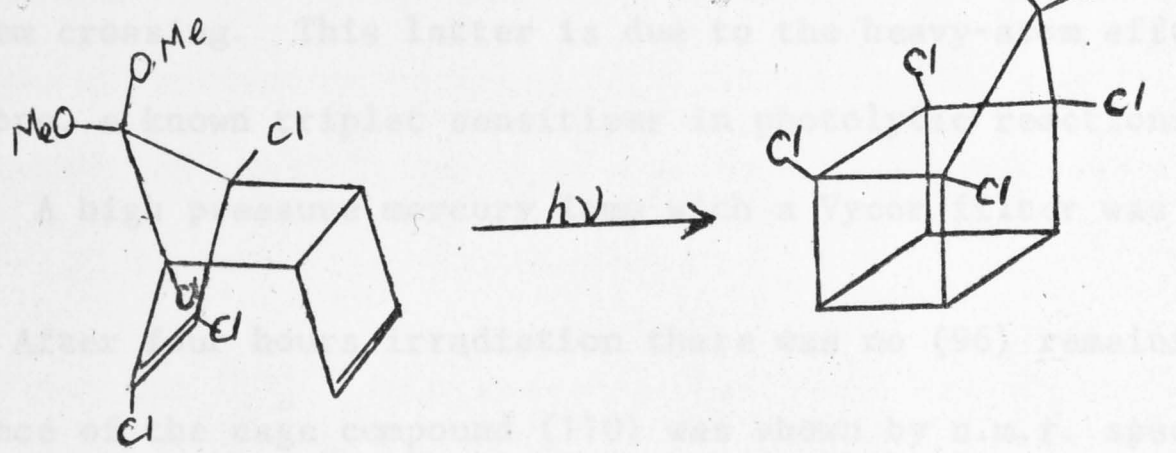
(106) (107)

(b)



(108) (109)

(c)



(96) (110)

the base of the doublet, was a multiplet covering a range of 18 cps. This was assigned to the cyclobutyl hydrogens. There was no vinyl signal in the n.m.r. spectrum of (110) at τ = 4.03 corresponding to that in the n.m.r. spectrum of the compound (96). It was therefore, considered that compound (96) was actually in the endo configuration and that a cage structure (110) had been formed on photolysis, cf. Diagram 18c.

It was apparent that the acetone solvent had acted as a triplet sensitiser in the photolysis of (96). To support this, a photolysis was carried out, using carbon tetrachloride as a solvent which would not act as a hydrogen donor in the possible dechlorination of (96), and also as a solvent which supports singlet to triplet (S - T) intersystem crossing. This latter is due to the heavy-atom effect. Benzophenone, a known triplet sensitiser in photolytic reactions was included. A high pressure mercury lamp with a Vycor filter was used.

After four hours irradiation there was no (96) remaining. The presence of the cage compound (110) was shown by n.m.r. spectroscopy. Attempts at complete removal of the benzophenone (111) from the photolysate were not successful. However, the n.m.r. spectra of (110) was in a different region, τ = 6.44, from that of benzophenone, τ = 2.40, and clearly characterised the compound.

A further confirmatory experiment on the triplet-triplet induced photo-cycloaddition of (96) to cage (110), with the inclusion of piperylene (112) to act as quencher for the triplet excitation, was not carried out owing to the exhaustion of the stock of (96).

The homocubane compound (110) is of some significance since it is readily obtained in two preparative stages from the starting materials and is only one stage away from a cubane system. Most cubane system syntheses have a number of involved preparative steps.

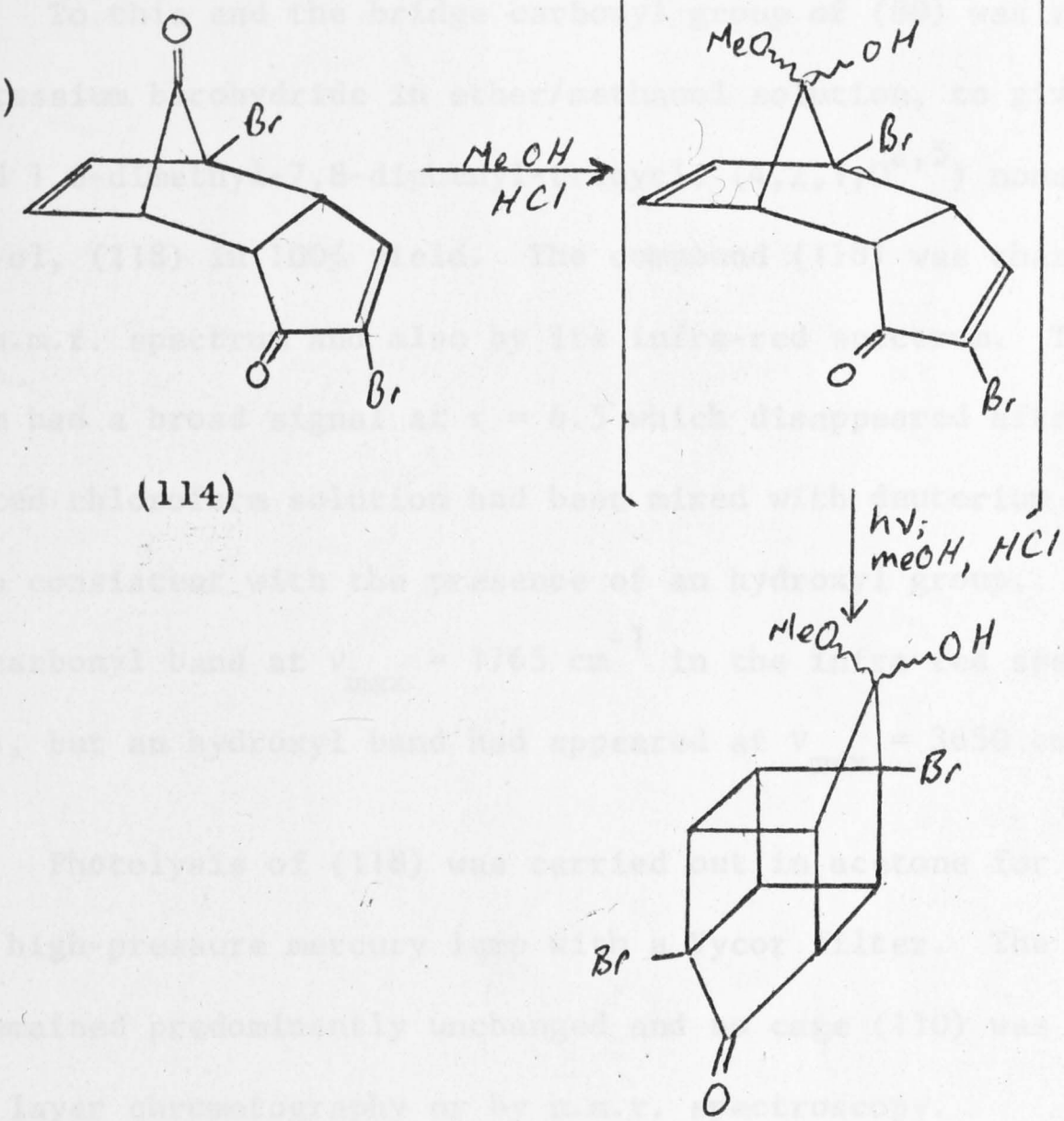
Pyrolysis of the cage compound (110) was carried out. It was stable when heated in a sealed tube under nitrogen at 200-210^{o} for 15 minutes, and when heated at 280^{o} for an hour, it partly charred with the production of hydrogen chloride. After removal of the charred material, some unchanged (110) was recovered, as evidenced by the n.m.r. spectrum.

With the successful photo-cycloaddition of (96) attention was again turned to the bridge-carbonyl compound (80). It was considered that if a way of preventing carbonyl elimination in (80) was found, photo-cycloaddition possibly could take place upon ultraviolet irradiation in acetone.

Eaton and Cole[40] have reasoned that their failure to obtain the caged-diketone (113) from (114) by irradiation in benzene was due to the sp^2 character of the one-carbon bridge in (114), cf. Diagram 19a. By irradiation in methonal containing hydrogen chloride they obtained the caged diketone (115). Diagram 19a. On the other hand, Griffin and Price[41] found that the diketone (116) upon irradiation through quartz or Pyrex gave (117) in good yield, cf. Diagram 19b.

DIAGRAM 19

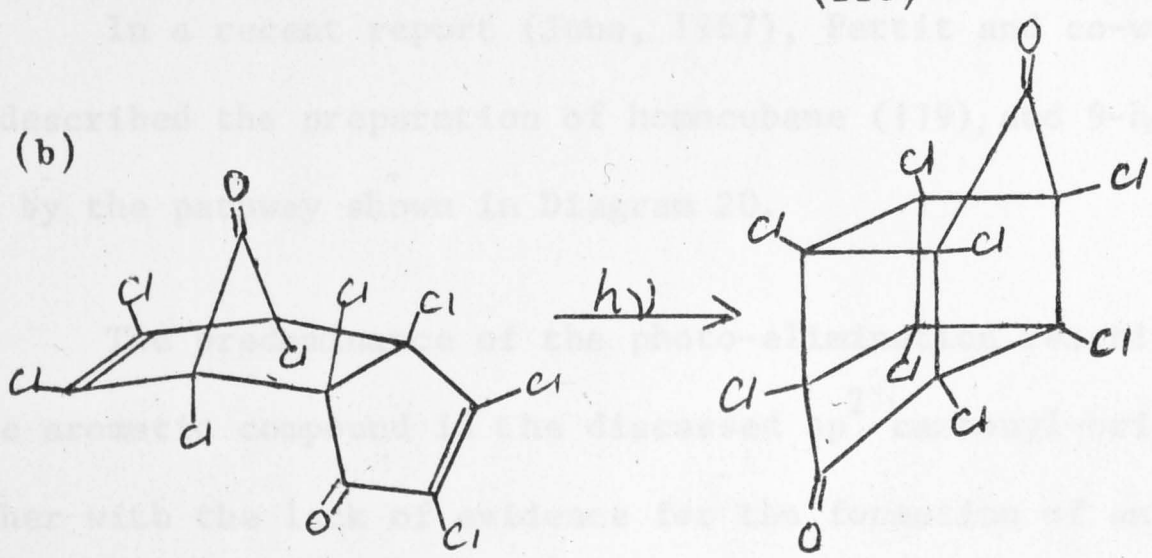
(a)



(114)

(115)

(b)



(116)

(117)

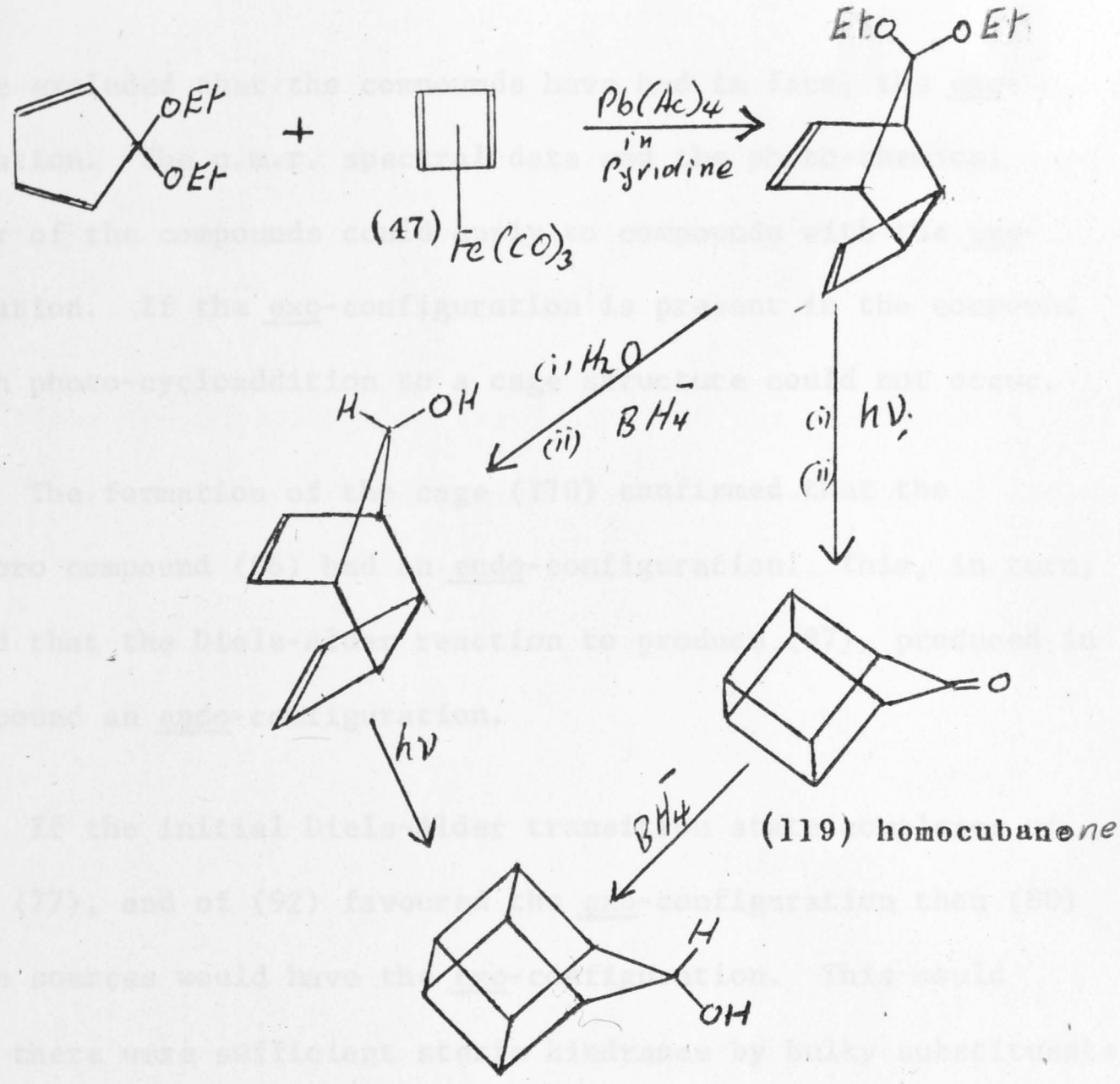
To this end the bridge carbonyl group of (80) was reduced with potassium borohydride in ether/methanol solution, to give the new compound 1,6-dimethyl-7,8-diphenyl-tricyclo (4,2,1,$0^{2,5}$) nona-3,7-diene-9-ol, (118) in 100% yield. The compound (118) was characterised by its n.m.r. spectrum and also by its infra-red spectrum. The n.m.r. spectrum had a broad signal at τ = 6.5 which disappeared after the deuterated chloroform solution had been mixed with deuterium oxide. This was consistent with the presence of an hydroxyl group. There was no carbonyl band at ν_{max} = 1765 cm^{-1} in the infra-red spectrum of (118), but an hydroxyl band had appeared at ν_{max} = 3650 cm^{-1}.

Photolysis of (118) was carried out in acetone for $3\frac{1}{2}$ hours, using a high-pressure mercury lamp with a Vycor filter. The compound (118) remained predominantly unchanged and no cage (110) was detected by thin layer chromatography or by n.m.r. spectroscopy.

In a recent report (June, 1967), Pettit and co-workers[42] have described the preparation of homocubane (119), and 9-homocubanol (120) by the pathway shown in Diagram 20.

The predominance of the photo-elimination reaction leading to the aromatic compound in the discussed sp^2 carbonyl-bridge compounds, together with the lack of evidence for the formation of any cage structure from (80) could lead to the conclusion that photo-elimination was the more favoured reaction for these compounds. There is however, the question of the stereochemistry of the compounds. The implication has been that they have had the <u>endo</u>-configuration, but the possibility

DIAGRAM 20



(119) homocubanone

(120) 9-homocubanol

cannot be excluded that the compounds have had in fact, the exo-configuration. The n.m.r. spectral data and the photo-chemical behaviour of the compounds could apply to compounds with the exo-configuration. If the exo-configuration is present in the compound (80) then photo-cycloaddition to a cage structure could not occur.

The formation of the cage (110) confirmed that the tetrachloro compound (96) had an endo-configuration. This, in turn, confirmed that the Diels-Alder reaction to produce (97), produced in this compound an endo-configuration.

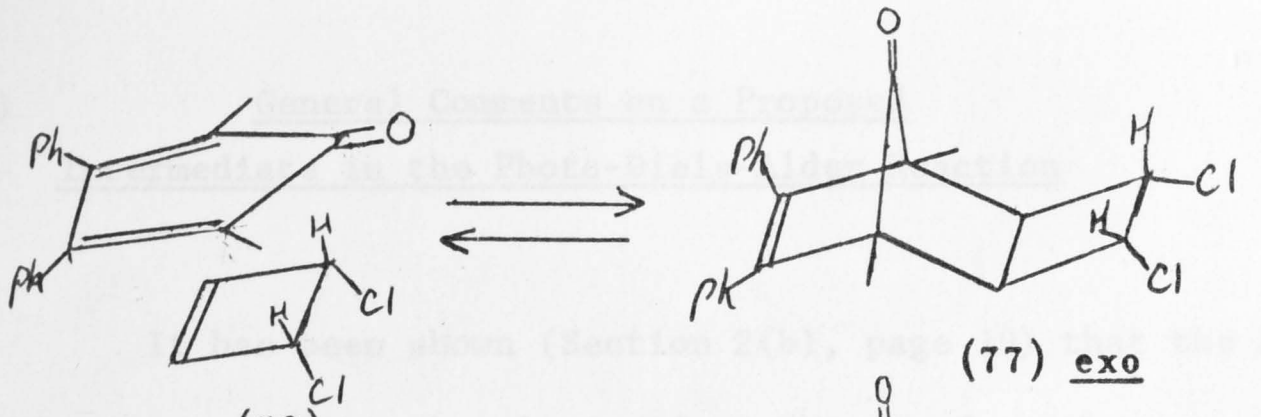
If the initial Diels-Alder transition state complexes of compound (77), and of (92) favoured the exo-configuration then (80) from both sources would have the exo-configuration. This could occur if there were sufficient steric hindrance by bulky substituents to prevent an endo approach of the diene to the dienophile.

In Diels-Alder reactions[43,44] dienophile substituents tend to be orientated in the favoured transition state so that they are directly above the unsaturated centres of the diene, either for reasons of maximum orbital overlap, or for reasons of steric accommodation. The transition state which is best stabilised by maximum orbital overlap, and is least destabilised by virtue of unfavourable steric repulsions has the lowest energy requirements, and therefore is the configuration which predominates in the kinetically determined product. There is, therefore, a strong propensity for most dienophile substituents to be

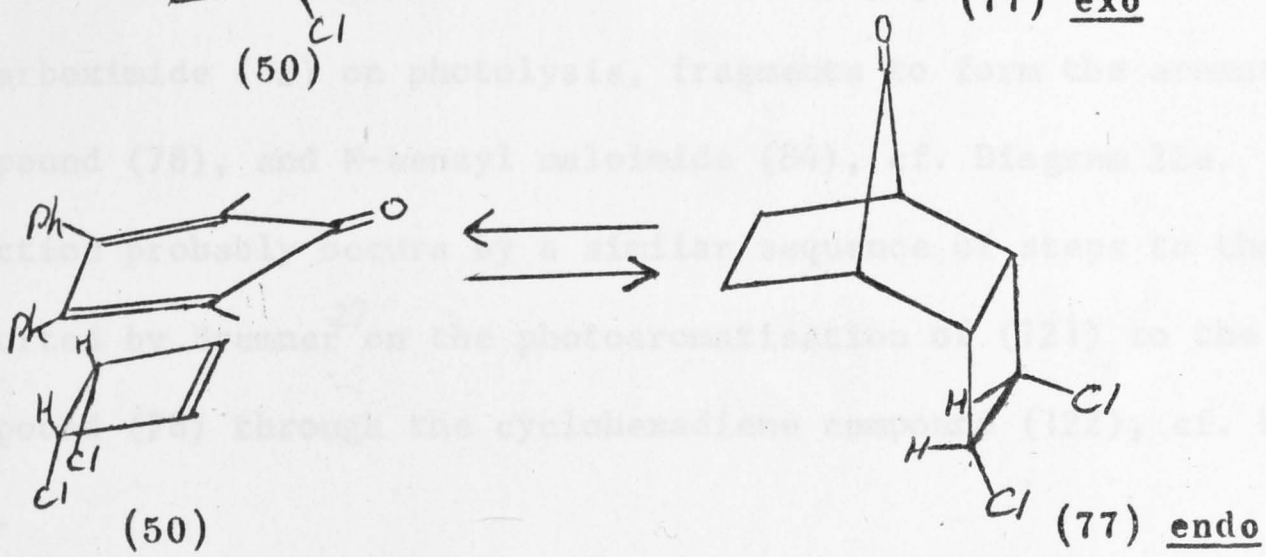
orientated in the endo-configuration in Diels-Alder adducts. There is also a general tendency for the diene, and dienophile to approach each other with a minimum of steric interaction. That is, from the less hindered side.

From the foregoing, an examination of the reactants in the Diels-Alder preparations (77), and (92) indicates that the steric factors in the reactions would have a significant role in the choice of final configuration of the product. Diagram 21 illustrates this.

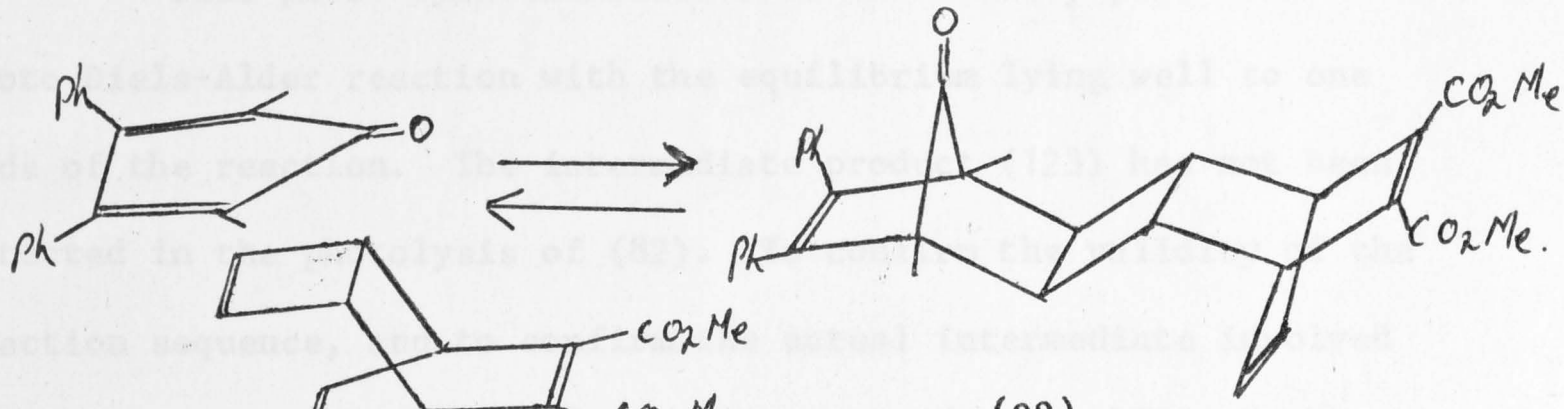
DIAGRAM 21



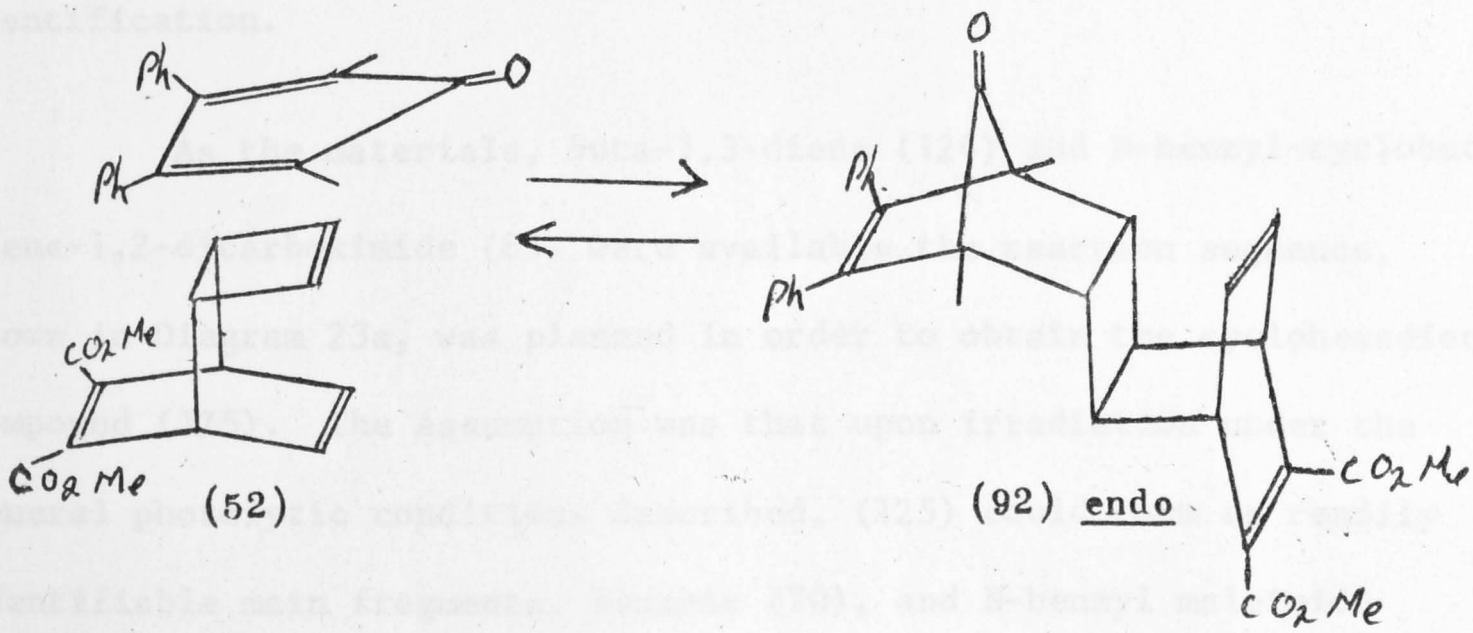
(50) (77) exo



(50) (77) endo



(52) (92) exo



(52) (92) endo

2(c) General Comments on a Proposed Intermediate in the Photo-Diels-Alder Reaction

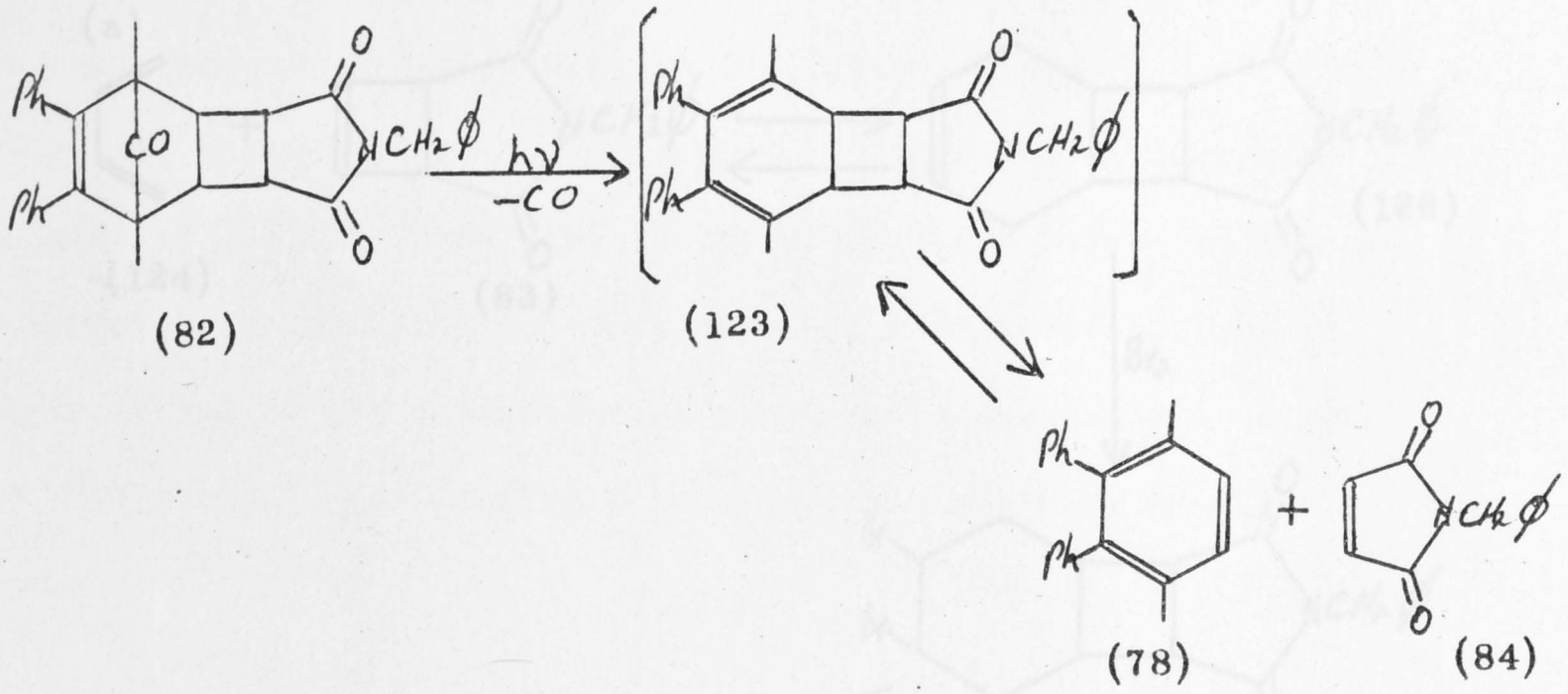
It has been shown (Section 2(b), page 19) that the N-benzyl dicarboximide (82) on photolysis, fragments to form the aromatic compound (78), and N-benzyl maleimide (84), cf. Diagram 22a. This reaction probably occurs by a similar sequence of steps to those reported by Bremner[27] on the photoaromatisation of (121) to the aromatic compound (78) through the cyclohexadiene compound (122), cf. Diagram 22b.

This photo-cycloelimination is essentially part of a photo-Diels-Alder reaction with the equilibrium lying well to one side of the reaction. The intermediate product (123) has not been detected in the photolysis of (82). To confirm the validity of the reaction sequence, and to confirm the actual intermediate involved it was of value to make a cyclohexadiene compound, establish its stereochemistry, and then irradiate it, trapping the products for identification.

As the materials, buta-1,3-diene (124) and N-benzyl-cyclobut-3-ene-1,2-dicarboximide (83) were available the reaction sequence, shown in Diagram 23a, was planned in order to obtain the cyclohexadiene compound (125). The assumption was that upon irradiation under the general photolytic conditions described, (125) could form as readily identifiable main fragments, benzene (70), and N-benzyl maleimide (84), cf. Diagram 23b.

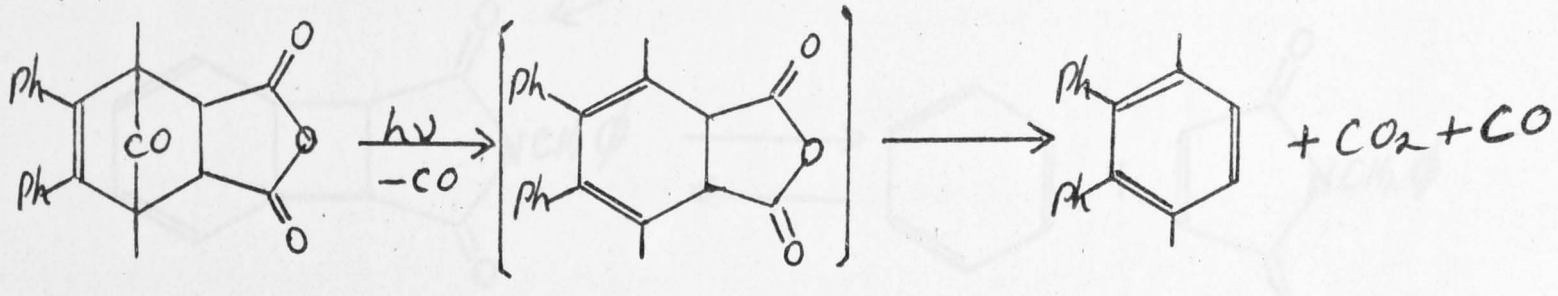
DIAGRAM 22

(a)



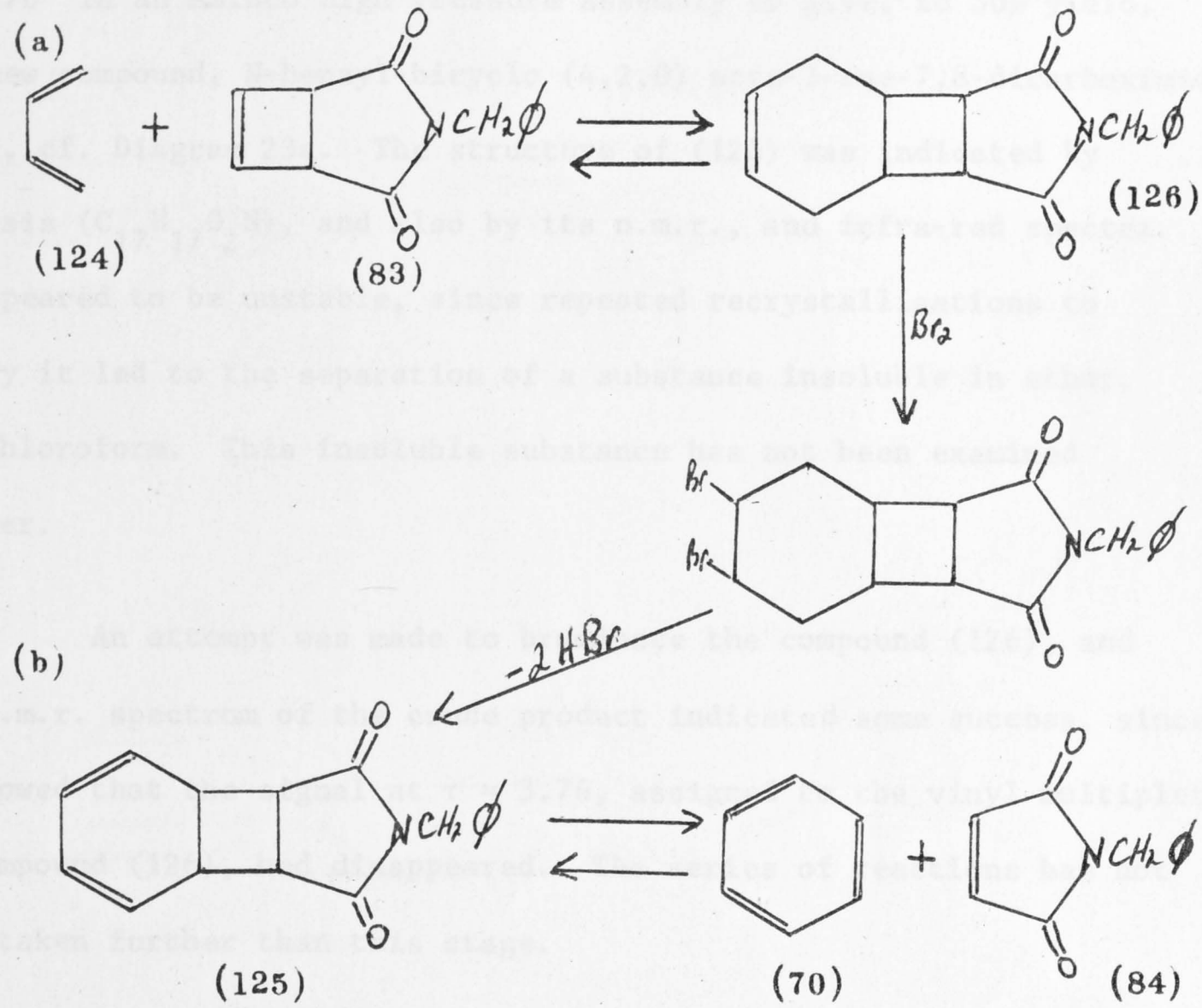
(82) (123) (78) (84)

(b)



(121) (78)

DIAGRAM 23



Buta-1,3-diene (124), and (83) were reacted together at 160-170^{o} in an Aminco High Pressure Assembly to give, in 30% yield, the new compound, N-benzyl-bicyclo (4,2,0) octa-3-ene-7,8-dicarboximide (126), cf. Diagram 23a. The structure of (126) was indicated by analysis ($C_{17}H_{17}O_2N$), and also by its n.m.r., and infra-red spectra. It appeared to be unstable, since repeated recrystallisations to purify it led to the separation of a substance insoluble in ether, and chloroform. This insoluble substance has not been examined further.

An attempt was made to brominate the compound (126), and the n.m.r. spectrum of the crude product indicated some success, since it showed that the signal at τ = 3.76, assigned to the vinyl multiplet of compound (126), had disappeared. The series of reactions has not been taken further than this stage.

An alternative means of gaining information about the configuration of the substituted cyclohexadiene compounds was to synthesise an analogous compound whose stereochemistry could be unambiguously determined. An attempt was made to overcome the problem by reacting (89), and cyclohex-3,5-diene,1,2-dicarboxylic anhydride (127)* in refluxing benzene to give the compound tricyclo (4,2,2,$0^{2,5}$) deca-7-ene-3,4,9,10-carboxylic-3,4,9,10-anyhdride (128), cf. Diagrams 24a and 24b. No doubt the compound (128) was obtained but attempts to purify it by recrystallisation resulted in its decomposition. The infra-red spectrum of (128) however was very similar to that of the analogous

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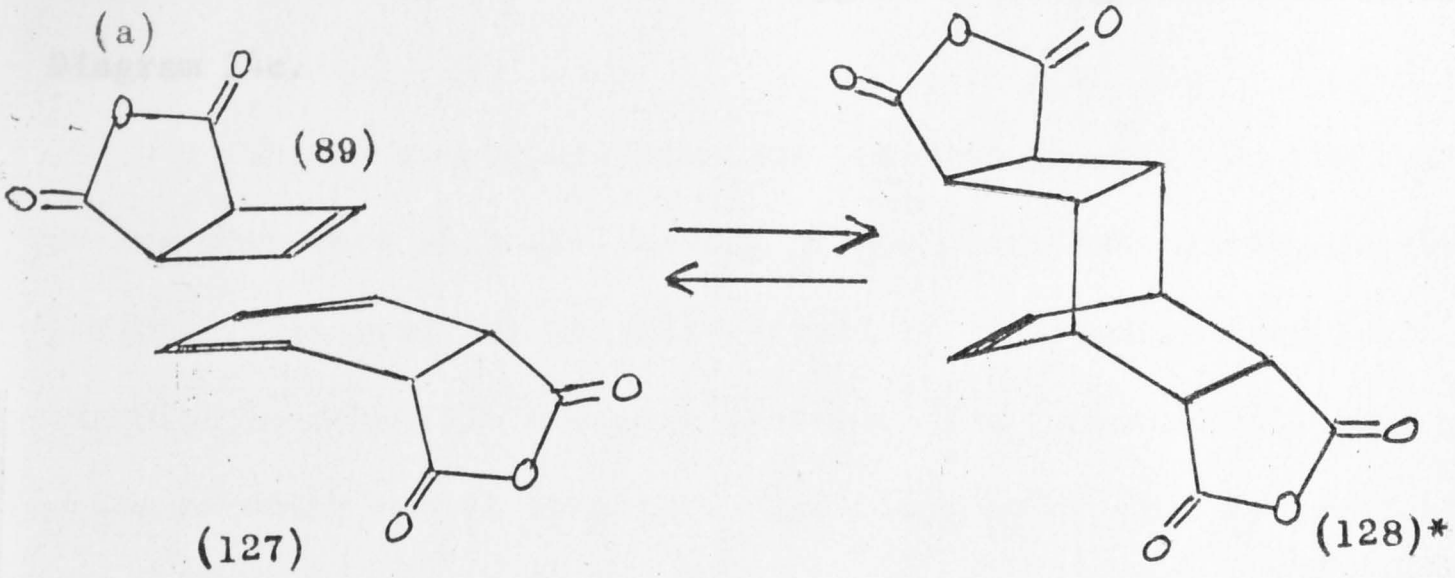
* Supplied by Dr. J.B. Bremner of this Department.

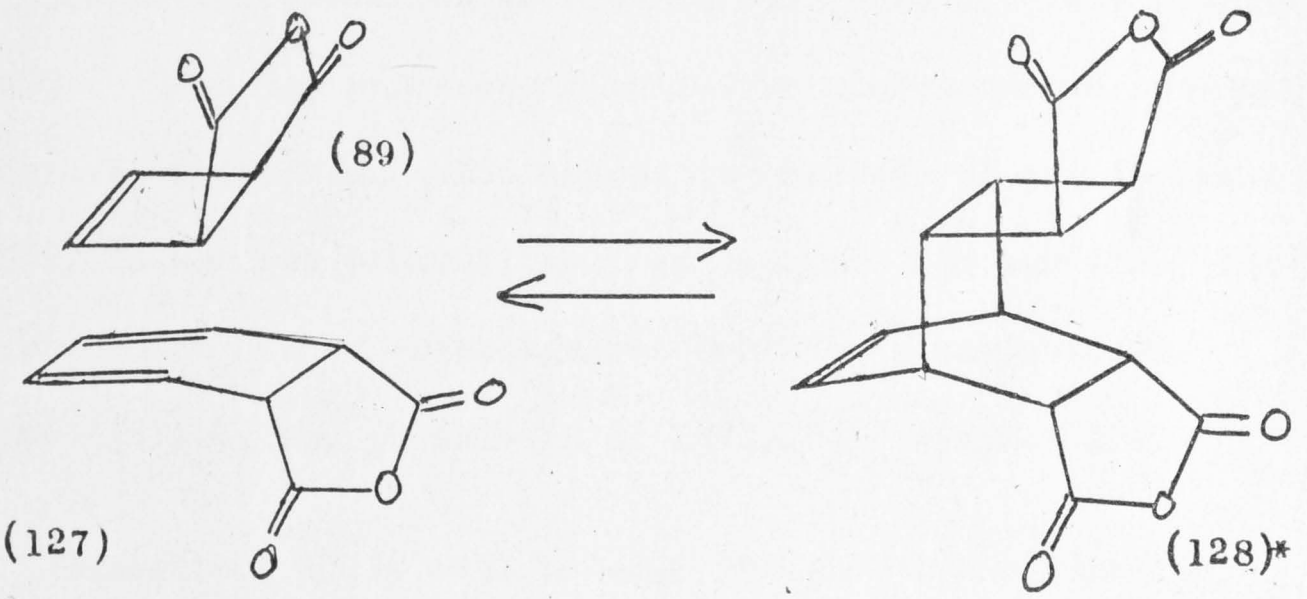
DIAGRAM 24

(a)



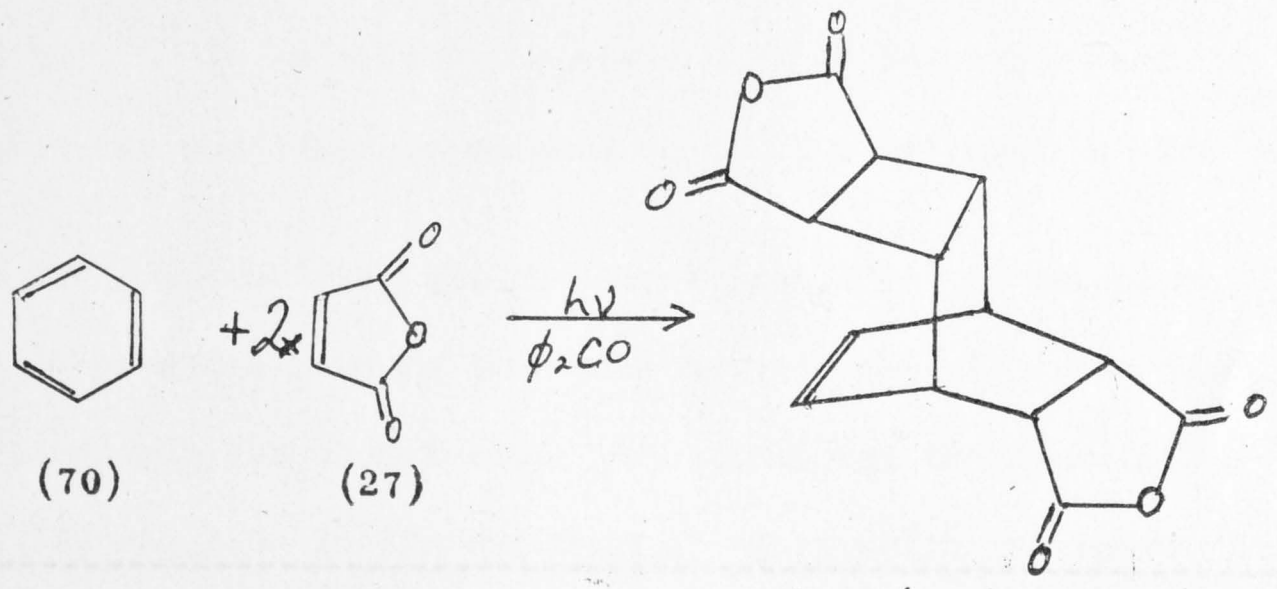
(89) (127) (128)*

(b)



(89) (127) (128)*

(c)



(70) (27) (129)

* Two of the possible isomers.

compound (129)*,[45] which has the suggested configuration shown in Diagram 24c.

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* Supplied by Dr. R.N. Warrener of this Department.

2(d) Applications of Photo-Cycloeliminations

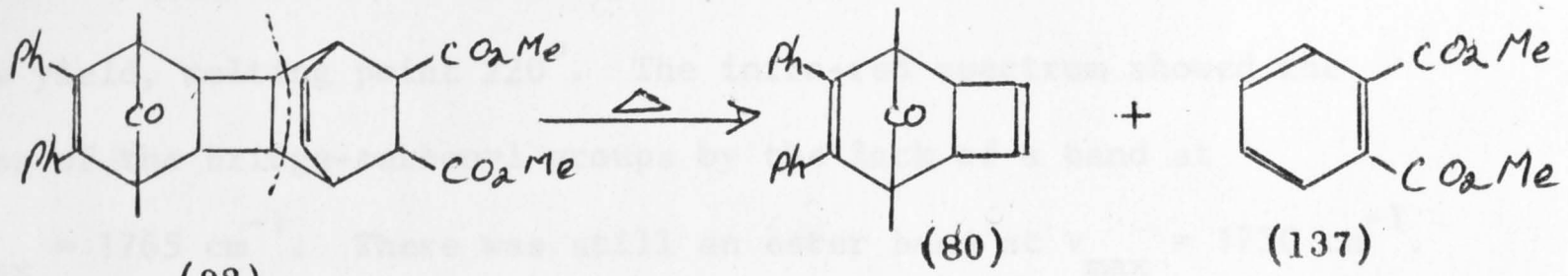
The photo-cycloelimination reaction seems to be the rule for the compounds with the leaving groups described earlier in this section. This reaction possibly, could be utilised to synthesise otherwise inaccessible bicyclic systems. The compound (92) was chosen as being one of interest. The cleavage of (92) by pyrolysis has been described (Section 2(b), page 21), but photolysis under selected conditions could follow a different route to yield a barrellene ester (130). That is, pyrolysis resulted in cleavage of a six-membered ring, whereas, photolysis could result in cleavage of the four-membered ring. This is set out schematically in Diagrams 25a and 25b. There is some precedent for the reaction, for Schröder[46] has obtained bullvalene (131) by the photolysis of (132), cf. Diagram 25d.

Barrellene (133) will undergo the photolytic reactions shown in Diagram 25e if irradiated with ultraviolet light of wavelength about 210 mμ .[47a] In an attempt to avoid this in the experiment, a Corex filter was used which precluded light of wavelength $\lambda \leqq 250$ mμ .

The compound (92) was photolysed for 17 hours in ether, using a high-pressure mercury lamp with a Corex filter. Five fractions were isolated from the photolysate. The first was the aromatic compound (78) obtained in 52% (of theory) yield which indicated, that a major reaction was that of cycloelimination.

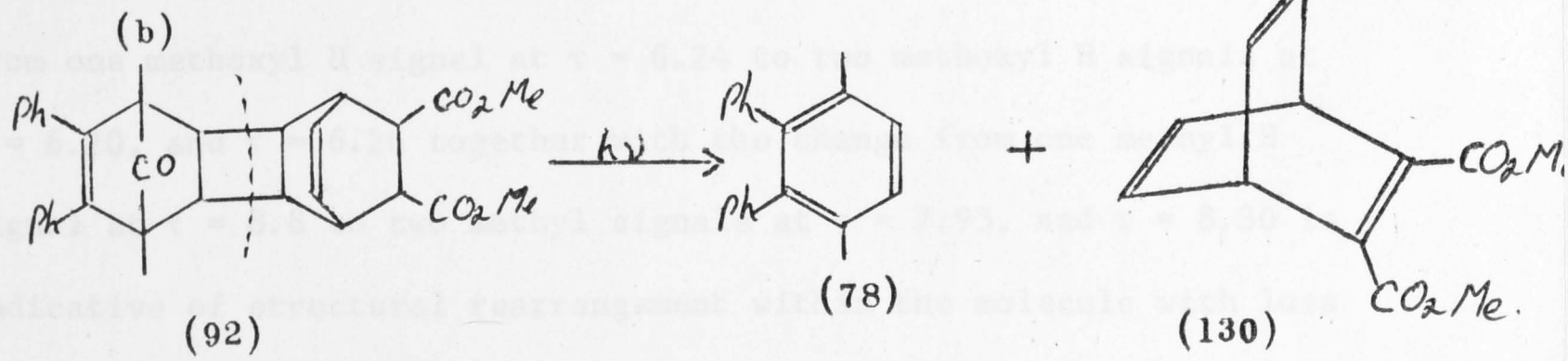
DIAGRAM 25

(a)



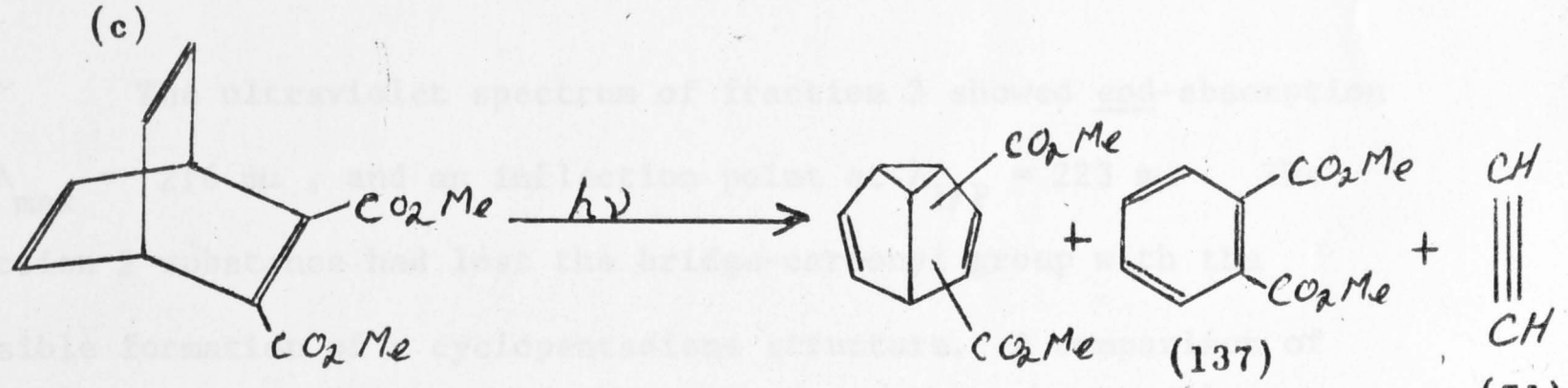
(92) (80) (137)

(b)



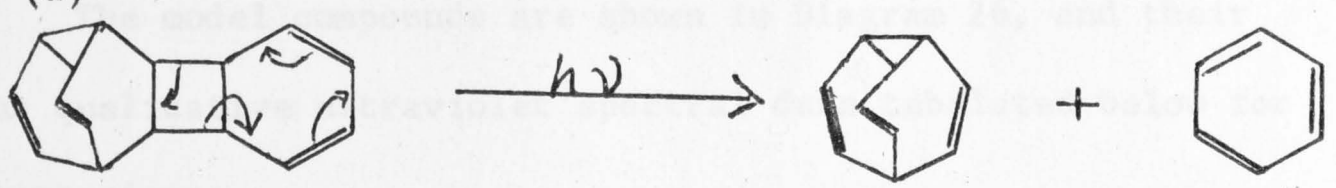
(92) (78) (130)

(c)



(130) (137) (71)

(d)



(132) (131) (70)

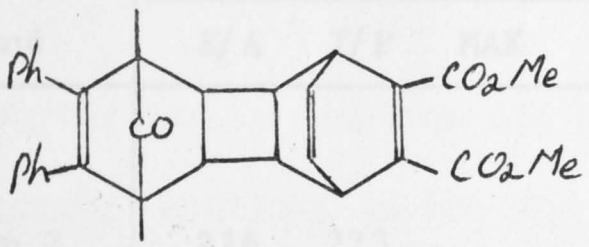
The second fraction was a white solid obtained in 10% w/w yield, melting point 220°. The infra-red spectrum showed the loss of the bridge-carbonyl groups by the lack of a band at ν_{max} = 1765 cm^{-1}. There was still an ester band at ν_{max} = 1730 cm^{-1}.

The n.m.r. spectrum has not been resolved, but the change from one methoxyl H signal at τ = 6.24 to two methoxyl H signals at τ = 6.20, and τ = 6.26 together with the change from one methyl H signal at τ = 8.8 to two methyl signals at τ = 7.95, and τ = 8.30 is indicative of structural rearrangement within the molecule with loss of symmetry.

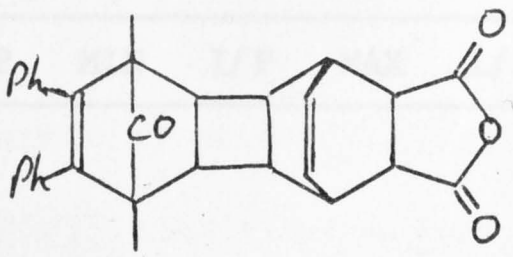
The ultraviolet spectrum of fraction 2 showed <u>end</u>-absorption at λ_{max} = 216 mμ , and an inflection point at $\lambda_{I/P}$ = 223 mμ . The fraction 2 substance had lost the bridge-carbonyl group with the possible formation of a cyclopentadiene structure. A comparison of its ultraviolet spectrum with those of model compounds showed that none of the spectra of the models resembled that of fraction 2 substance.

The model compounds are shown in Diagram 26, and their relevant qualitative ultraviolet spectral data tabulated below for ready comparison:

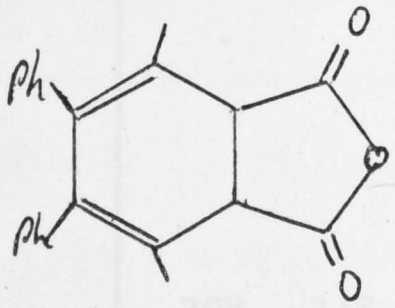
DIAGRAM 26



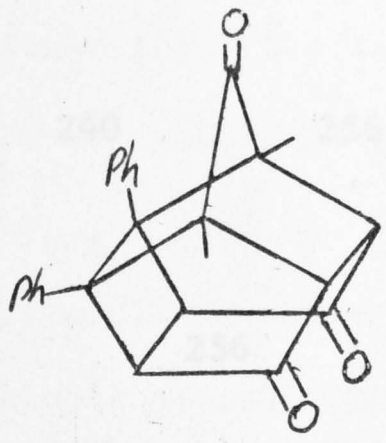
(92)



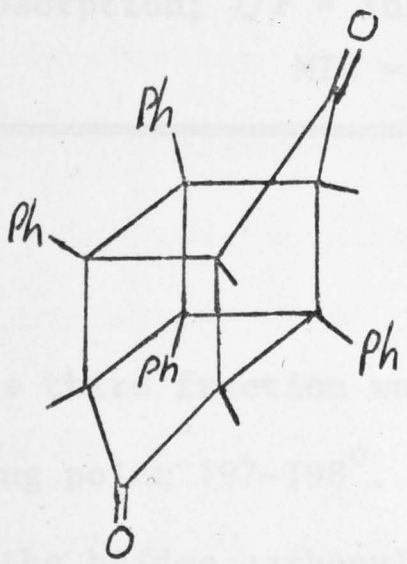
(177)



(178)



(179)



(180)

Compound	Increasing wavelength (mμ) ⟶								
	E/A	I/P	MAX	I/P	MIN	I/P	MAX	L/P	I/P
Fraction 2	216	223							
(92)	209		225	250					
(177)	210	220			240		256		
(178)			225	235				263	
(179)			223			256			
(180)	208	218			241			263	285

E/A = end absorption; I/P = inflection point; MAX = maximum; and MIN = minimum.

The third fraction was a white solid obtained in 5% w/w yield, melting point 197-198°. The infra-red spectrum demonstrated the loss of the bridge carbonyl group by the lack of a band at ν_{max}: 1765 cm^{-1}. There was still an ester band at ν_{max}: 1715 cm^{-1}.

The n.m.r. spectrum was essentially the same as the starting compound (92) except for slight shifts down, or up field of the signals. The ratio of peak integrations was 5.75:1:1:3:1:1:3 whereas that of (92) is 5:1:1:3:1:1:3. This difference in the aromatic region could

be due to the presence of a small amount of an aromatic compound impurity.

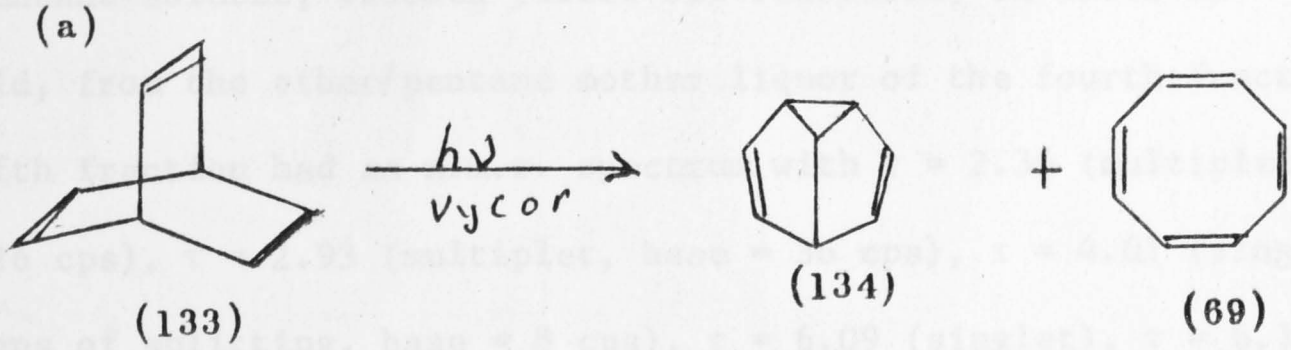
The fourth fraction was obtained by precipitation from an ether/pentane solution, in 48% w/w yield, as an ether-soluble, white, fluffy powder which melted over the range 115-127°. The n.m.r. spectrum had no distinguishable characteristics. The infra-red spectrum had a broad band at ν_{max}: 1730 cm^{-1} indicative of an ester carbonyl, and two other broad bands at ν_{max}: 1270 cm^{-1}, and ν_{max}: 730 m cm^{-1}. The infra-red spectrum did not have bands in the ν_{max} = 700 region indicative of aromatic groups. The ultraviolet spectrum showed no maxima. There was end-absorption past λ_{max}: 220 mμ, and an inflection point at $\lambda_{I/P}$ = 250 mμ, and at $\lambda_{I/P}$ = 330 mμ.

It is probable that this last fraction consisted of material which had been cycloeliminated from compound (92) during the photolysis. It was not the desired barrellene ester (130), nor an ester derivative (134) of semibullvalene (135) to which barrellene is isomerised upon irradiation.

Zimmermann and Grunewald[47b] have recently shown that barrellene (133) is converted to the semi-bullvalene structure (134) upon irradiation through a Vycor filter, cf. Diagram 27a. Maitland Jones and Scott[48] have reported the synthesis of the related (136), and its conversion to bullvalene (131) upon irradiation with ultraviolet light. Conversion is slow with a Pyrex filter and rapid with a Quartz filter, cf. Diagram 27b.

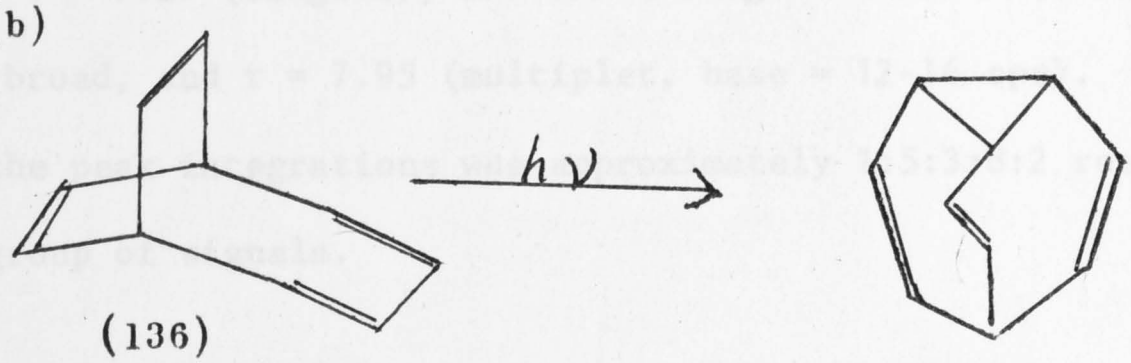
DIAGRAM 27

(a)



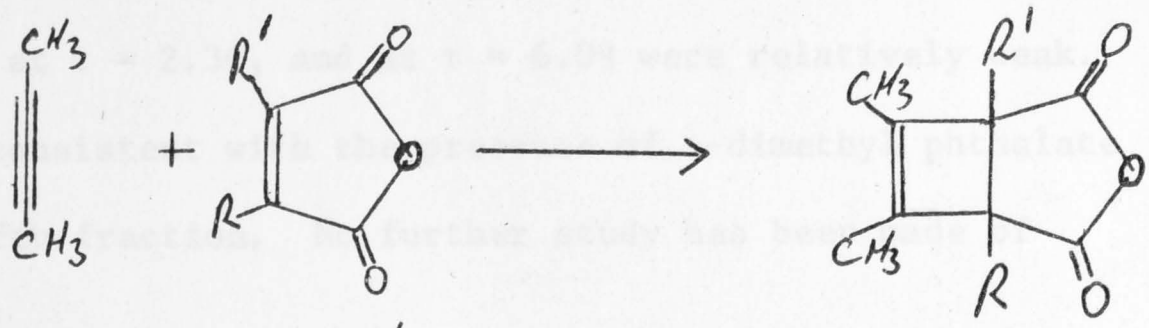
(133) (134) (69)

(b)



(136) (131)

(c)



(i) $R = R' = H$;

(ii) $R = H, R' = CH_3$;

(iii) $R = R' = CH_3$.

The fifth fraction obtained from the irradiation of (92) was a pentane-soluble, viscous yellow oil recovered, in about 5% w/w yield, from the ether/pentane mother liquor of the fourth fraction. This fifth fraction had an n.m.r. spectrum with τ = 2.36 (multiplet, base = 16 cps), τ = 2.93 (multiplet, base = 36 cps), τ = 4.01 (singlet with signs of splitting, base = 8 cps), τ = 6.09 (singlet), τ = 6.16 (singlet), τ = 7.27 (singlet), all three singlets from a common base, 20-22 cps broad, and τ = 7.95 (multiplet, base = 12-14 cps). The ratio of the peak integrations was approximately 1:5:3:8:2 respectively, for each group of signals.

An inspection of the n.m.r. spectrum showed that the signals at τ = 2.93, τ = 4.01, and τ = 7.27 were much stronger than those in the remainder of the spectrum. They were assigned as aromatic H, vinyl H, and methoxyl H, respectively. Compared with these by inspection, the signals at τ = 2.36, and at τ = 6.09 were relatively weak. They were not inconsistent with the presence of o-dimethyl phthalate (137), in the fifth fraction. No further study has been made of this fraction.

Although the experiment was unsuccessful in that the desired (130) was not obtained, the recovery of aromatic compound (78) in good yield showed that the major photolytic reaction was cleavage of the cyclobutane ring with photoaromatisation of one fragment to give (78), with attendant photoelimination of the other fragment which yielded secondary photolytic products. At most,

the experiment promised that (130) could be obtained, given the right photolytic conditions of intensity of irradiation, duration of irradiation, and ultraviolet wavelength range.

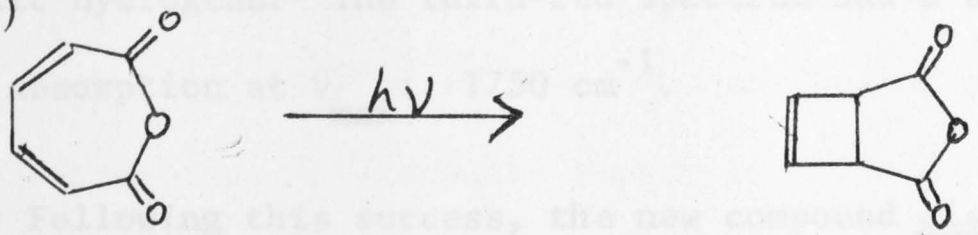
2(e) Low Temperature Photo-Cycloaddition Compounds and Derivatives

The photo-cycloaddition in the presence of benzophenone of maleic anhydride (27) and derivatives, to 2-butyne was described by Criegee and co-workers[49] in 1964, cf. Diagram 27c. Koltzenberg and co-workers[13] (in 1966) reported the first successful photo-cycloaddition at low temperature (-51^{o}) of acetylene (71), and maleic anhydride (27) to give the 1:1 adduct, cyclobut-3-ene 1,2 dicarboxylic anhydride (89), cf. Diagram 28a. At room temperature the product was mainly the 1:2 adduct (138), cf. Diagram 28b. The compound (89) was first described in a short communication by Fonken[50] who prepared it by irradiating muconic anhydride in ether, cf. Diagram 28c.

Since (89) is of considerable interest, attempts were therefore made to prepare it according to Koltzenberg's brief description of his method. It was isolated in 49% yield, and its structure was confirmed by its n.m.r., and infra-red spectra. Its melting point was 88^{o}. (Literature 90^{o}.) The n.m.r. spectrum had τ = 3.42 (2H, singlet) which was assigned to the vinyl hydrogens, and τ = 5.93 (2H, singlet), which was assigned to the tertiary hydrogens. The signals were sharp with no apparent splitting. The widths at half-height ($W_{\frac{1}{2}}$) for the vinyl hydrogens, and for the methine hydrogens were respectively, 2 cps, and 3 cps with reference to trimethylsilane $W_{\frac{1}{2}}$ = 1 cps. This approximation was consistent with a low degree of coupling between the methine hydrogens, and

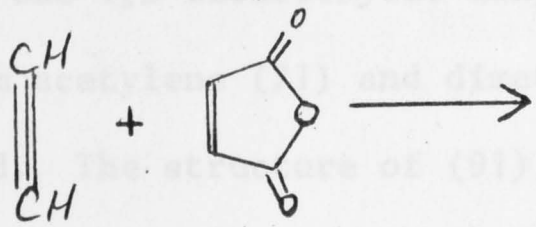
DIAGRAM 28

(c)



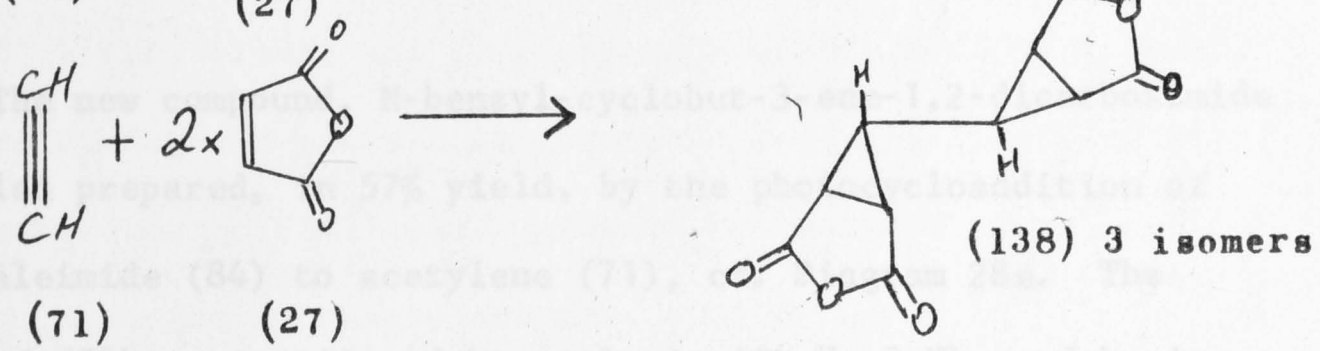
(89)

(a)



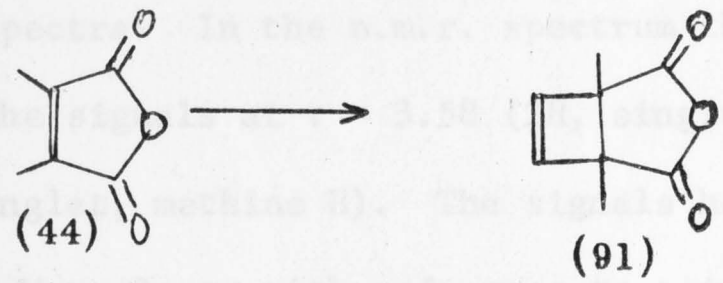
(71) (27) (89)

(b)



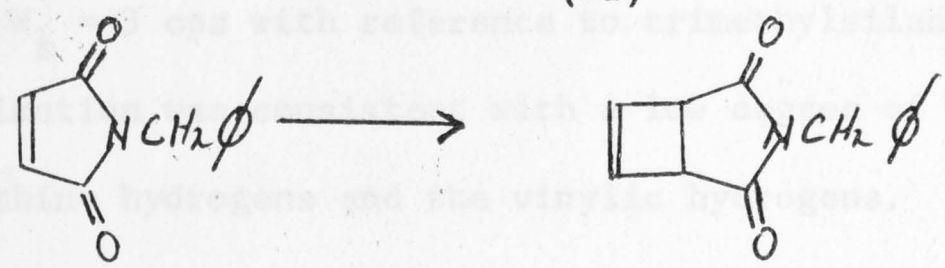
(71) (27) (138) 3 isomers

(d)



(71) + (44) (91)

(e)



(71) + (84) (83)

the vinylic hydrogens. The infra-red spectrum had a strong anhydride carbonyl absorption at ν_{max} : 1750 cm^{-1}.

Following this success, the new compound cis-1,2-dimethyl-cyclobut-3-ene-1,2-dicarboxylic anhydride (91) was prepared in 43% yield, from acetylene (71) and dimethyl maleic anhydride (44), cf. Diagram 28d. The structure of (91) was confirmed by analysis (C_8H_8O), and also by its n.m.r. and infra-red spectrum.

The new compound, N-benzyl-cyclobut-3-ene-1,2-dicarboximide (83) was also prepared, in 57% yield, by the photocycloaddition of N-benzyl maleimide (84) to acetylene (71), cf. Diagram 28e. The structure of (83) was confirmed by analysis ($C_{13}H_{11}O_2N$), and by its n.m.r., and infra-red spectra. In the n.m.r. spectrum there was no apparent splitting of the signals at τ = 3.58 (2H, singlet, vinyl H) and at τ = 6.21 (2H, singlet, methine H). The signals had vinyl $W_{\frac{1}{2}}$ = 3 cps, and methine $W_{\frac{1}{2}}$ = 3 cps with reference to trimethylsilane $W_{\frac{1}{2}}$ = 2cps. This approximation was consistent with a low degree of coupling between the methine hydrogens and the vinylic hydrogens.

In contrast to the preparation of (83), Koltzenberg and co-workers[13] reported that they were unable to obtain the 1:1 adduct N-phenyl-cyclobut-3-ene 1,2 dicarboximide (138) from cycloaddition at low temperature of N-phenyl maleimide (198) to acetylene (71). Instead they obtained the dimer of (198). They, however, were able to obtain the 1:1 adducts of N-ethyl-maleimide, and of maleimide.

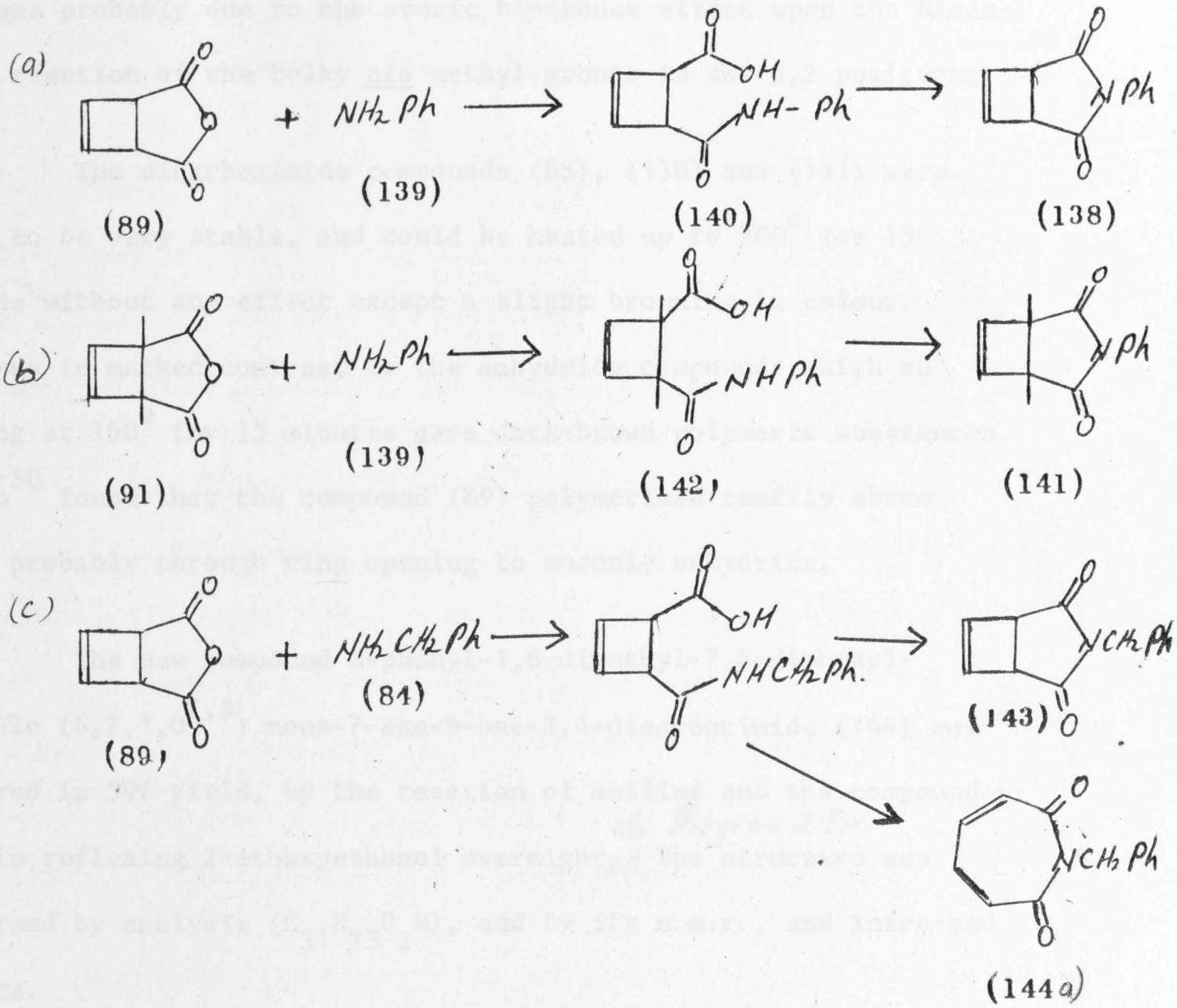
The new compound, N-phenyl-cyclobut-3-ene 1,2-dicarboximide (138) was prepared in 26% yield from the reaction of aniline (139), and (89), through the intermediate N-phenyl-cyclobut-3-ene 1,2-dicarboxamic acid (140), cf. Diagram 29a. The structure was confirmed by analysis ($C_{12}H_9O_2N$) and by its n.m.r., and infra-red spectra.

Similarly the new compound, N-phenyl-cis-1,2-dimethyl-cyclo-but-3-ene 1,2-dicarboximide (141) was prepared from the reaction of aniline (139), and (91) through the intermediate N-phenyl-1,2-dimethyl cyclobut-3-ene 1,2 dicarboxamic acid (142), cf. Diagram 29b. The structure of (141) was confirmed by analysis ($C_{14}H_{13}O_2N$) and by its n.m.r. and infra-red spectra.

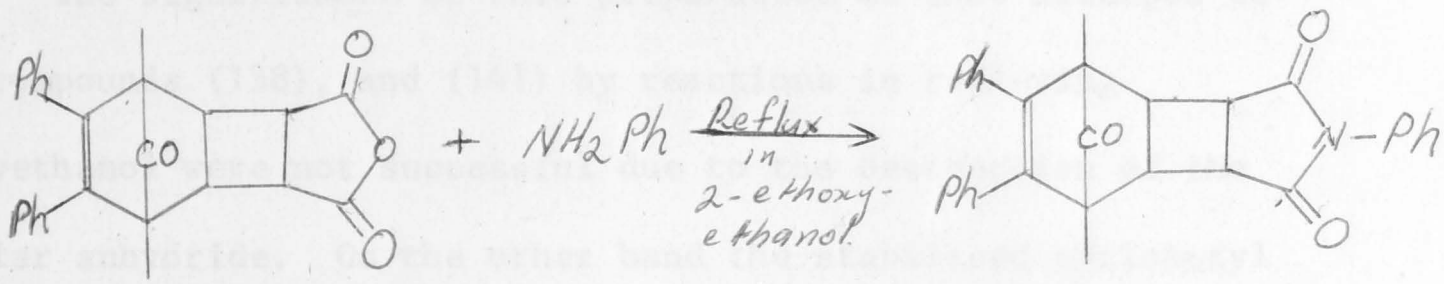
An attempt was made to prepare the compound N-benzyl-1,2-dimethyl-cyclobut-3-ene 1,2-dicarboximide (143) in the manner described but while the n.m.r. spectrum indicated that the reaction was successful, the compound was not obtained pure, cf. Diagram 29c. A small amount of what was considered to be N-benzyl-1,4-dimethyl-muconimide (144a) was also present. This could account for the small, but observable n.m.r. signals at τ = 5.51, τ = 8.61, and at τ = 7.95.

The compounds appear, in general, to be good dienophiles as shown by the use of (89) to make (90) under mild conditions, and the use of (83) to make (82), and (126). The latter reaction was carried out at 160°. (Section 2(b), pages 20,32.) The exception was the dimethyl compound (91) which broke down instead of reacting.

DIAGRAM 29



(d)



(90) (139) (144)

This was probably due to the steric hindrance effect upon the Diels-Alder reaction of the bulky cis methyl-groups in the 1,2 positions.

The dicarboximide compounds (83), (138) and (141) were found to be very stable, and could be heated up to 300° for 15 minutes without any effect except a slight browning in colour. This was in marked contrast to the anhydride compounds which on heating at 160° for 15 minutes gave dark-brown polymeric substances. Fonken[50] found that the compound (89) polymerised readily above 100°, probably through ring opening to muconic anhydride.

The new compound N-phenyl-1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one-3,4-dicarboximide (144) was prepared in 59% yield, by the reaction of aniline and the compound (90) in refluxing 2-ethoxyethanol overnight, cf. Diagram 29d. The structure was confirmed by analysis ($C_{31}H_{25}O_2N$), and by its n.m.r., and infra-red spectra.

The significance of this preparation is that attempts to obtain compounds (138), and (141) by reactions in refluxing 2-ethoxyethanol were not successful due to the destruction of the particular anhydride. On the other hand the stabilised cyclobutyl anhydride system of (90) was successfully converted to the dicarboximide.

The compounds (89), (91), (83), (138), and (141) are further described in the Section 3 on Mass Spectral Studies.

2(f) The Stereochemistry of 2-Methyl-1,4-Naphthoquinone Dimer (1)

Madinaveitia[1] first reported in 1933 that the compound (1) formed a photo-product upon exposure to sunlight. He suggested that it was dimeric and assigned the following structure: 2,3,2',3'-tetra hydro-2,3-dimethyl-2,3,2',3'-binaphthylene-1,4,1',4'-tetrone.

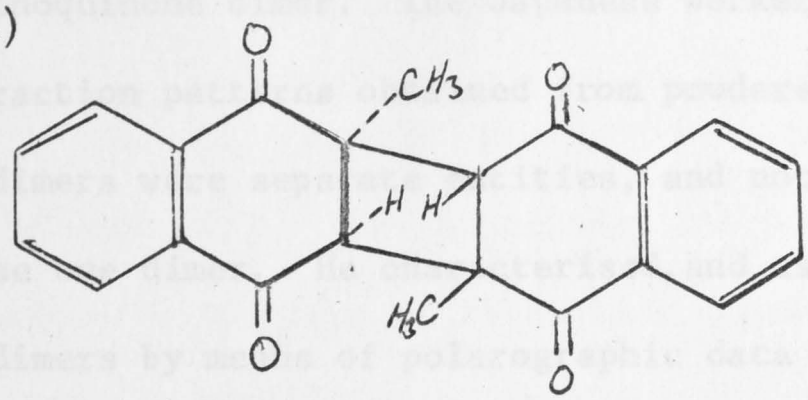
Yutaka Asahi[2] reported the isolation of 2 dimers of (1), obtained by the irradiation of (1) in dilute ethanolic solution in the presence of oxygen. These two dimers were obtained through the intermediary 2-methyl-3,4-epoxy-1,4-naphthoquinone (2) formed during the irradiation. He assigned the structures (3), and (4) shown in Diagrams 30a and 30b. It is not certain whether the Japanese worker also obtained the two dimers from a solid state irradiation of (1).

Excluding trans-fused ring structures there are four possible isomers of the dimer depending on the positions of the two methyl groups in the cyclobutane ring, and the manner in which the naphthoquinonoid moieties are attached to the ring. These isomers can have the two methyls in the positions cis-1,2-, cis-1,3-, trans-1,2-, and trans-1,3-dimethyl respectively. These are shown in Diagram 30.

There was sufficient doubt on the basis of the assigned structures and different also on irradiation procedure in ethanol as to whether one of the two dimers obtained by Yutaka Asahi was identical with the dimer obtained from the solid state irradiation

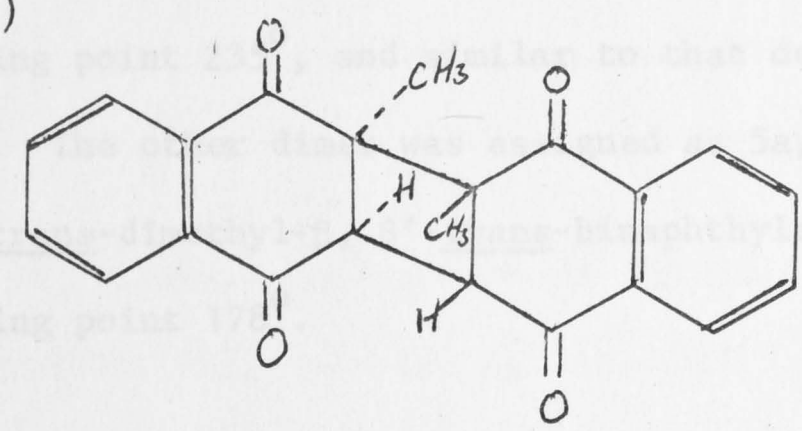
DIAGRAM 30

(a)



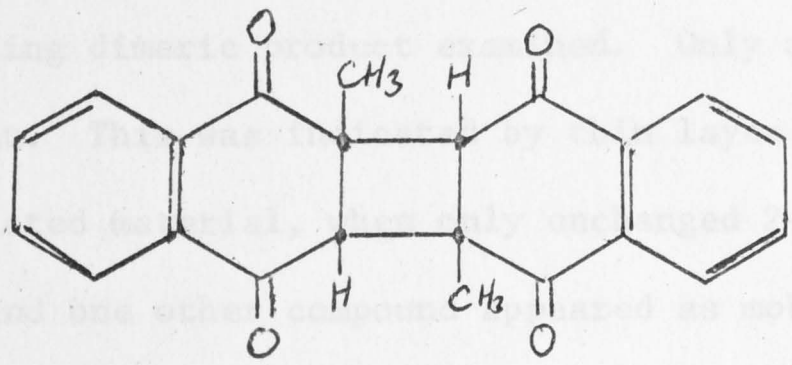
(3)

(b)



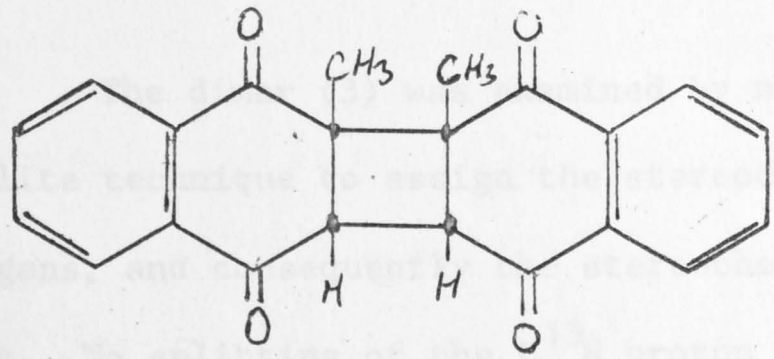
(4)

(c)



(5)

(d)



(6)

by Madinaveitia, to warrant further study on the 2-methyl naphthoquinone dimer. The Japanese worker by means of x-ray diffraction patterns obtained from powdered material, showed that the two dimers were separate entities, and not merely two crystal forms of the one dimer. He characterised, and assigned the structure of the dimers by means of polarographic data and infra-red spectroscopy. One dimer, was assigned the structure 5a, 5b, 11a, 11b-tetrahydro-5a, 11a-trans-dimethyl β, β′-trans-binaphthylene-5,6,11,12-tetrone (3), melting point 235°, and similar to that described by Madinaveita in 1933. The other dimer was assigned as 5a, 5b, 11a,11b-tetrahydro-11a, 11b-trans-dimethyl-β, β′-trans-binaphthylene-5,6,11,12 tetrone (4), melting point 178°.

In the continuing study (1) was irradiated in the solid state by a battery of four 15-watt black-light lamps, and the resulting dimeric product examined. Only one dimer appeared to be present. This was indicated by thin layer chromatography of the irradiated material, when only unchanged 2-methyl-1,4-naphthoquine (1), and one other compound appeared as mobile spots. The dimer was obtained in 90% yield, melting point 234°, and had an infra-red spectrum similar to that depicted by Yutaka Asahi for (3).

The dimer (3) was examined by n.m.r. using the $C^{13}H$ satellite technique to assign the stereochemistry of the cyclobutane hydrogens, and consequently the stereochemistry of the two methyl groups. No splitting of the $C^{13}H$ proton signals was observed, which

was consistent with the methyl-groups being on the cyclobutane ring in the 1,3-positions, and probably, in the trans-configuration.*

So far there is agreement with the Japanese workers' structure for the dimer (3). However neither the n.m.r. spectral studies, nor the infra-red spectrum of this dimer can differentiate between the structure (3) postulated by Yutaka Asahi and the postulated structure shown in Diagram 31.

The circumstantial evidence pointing to this postulated double-oxetan structure (145) is developed as follows.

Cookson and co-workers[5] irradiated 2,6 dimethyl-1,4-benzoquinone (9), and also 2,5 dimethyl 1,4-benzoquinone (14). They obtained what were first thought to be two cyclobutane ring dimers for each starting quinone. Thus, they obtained in 70% yield a trans, 1,2-dimethyl-dimer (12), and a cis-1,3 dimethyl-dimer (10) in 5% yield from the quinone (9). They also obtained a trans-1,3-dimethyl-dimer (13) in 40% yield, and a cage-dimer in 2% yield from the quinone (14).

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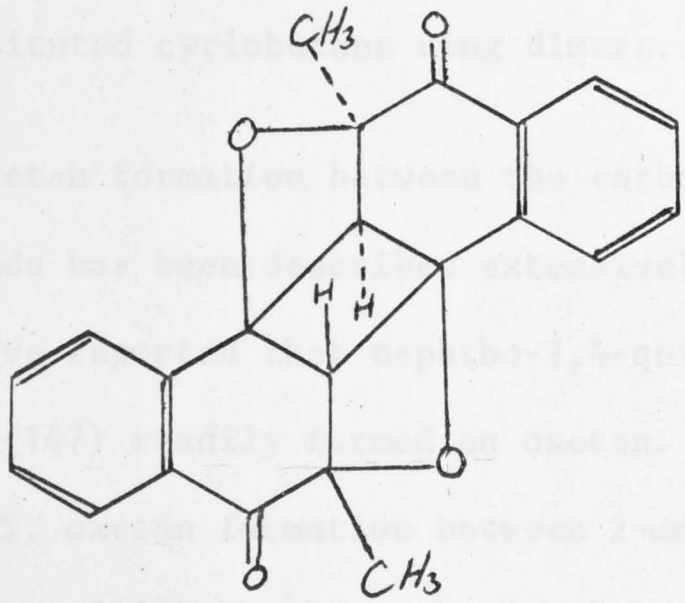
* The n.m.r. $C_{13}H$ satellite spectral studies were carried out by Dr. T. Batterham of the John Curtin School of Medical Research, Canberra, A.C.T.

DIAGRAM 31



(145)

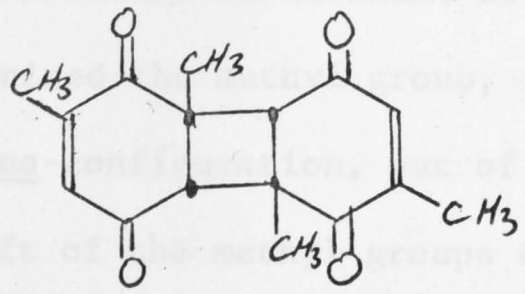
The structures for (12), and (13) were subsequently withdrawn by Cookson[6] to be replaced by their respective oxetan structures (15), and (16), cf. Diagram 32. These were the products obtained in high yields in contrast to 5% and 2% yields respectively, of the substituted cyclobutane ring dimers.

Oxetan formation between the carbonyls of quinones, and olefinic bonds has been described extensively. Bryce-Smith and Gilbert[51] have reported that naphtho-1,4-quinone (146) and cis-cyclooctene (147) readily formed an oxetan. In this thesis, Section 2(g), page 55, oxetan formation between 2-methyl naphthoquinone (1) and cyclohexene (148) has been shown, although the oxetan has not been completely characterised.

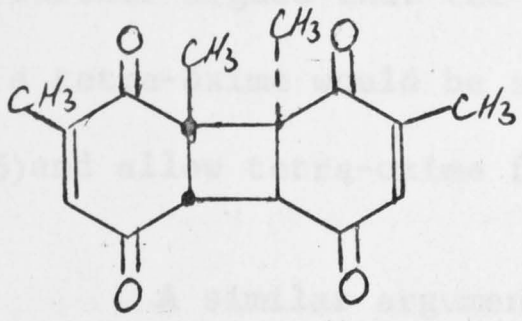
In view of these data, the possibility cannot be overlooked that (1) can form oxetan structures similar to those described by Cookson and co-workers[6] for (9), and (14), although such oxetan structures have not been reported in the literature. Recently Scharf and Korte[62] reported the formation of the internal oxetan (177) from the compound (178) by irradiation, cf. Diagram 32.

In opposition to the double-oxetan structure (145) postulated, is the fact that Madinaveitia obtained a tetra-oxime from the reaction of hydroxylamine (149) and dimer (3). The compound (1) yields a monoxime (150) when reacted with (149). It is argued that the methyl group in the 2-position in (1) is in the plane of the quinonoid ring

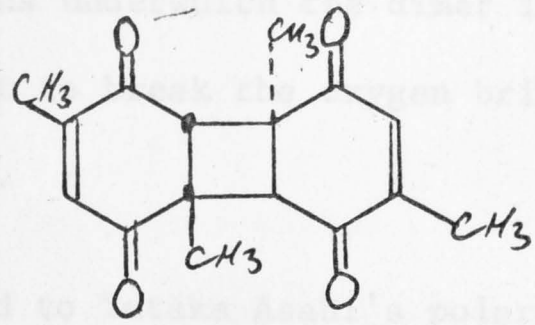
DIAGRAM 32



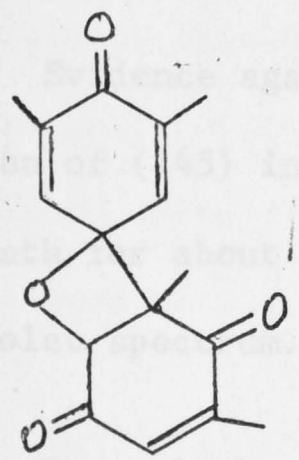
(10)



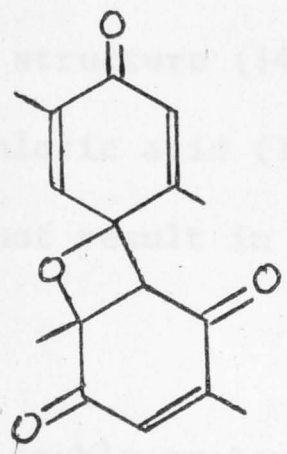
(12)



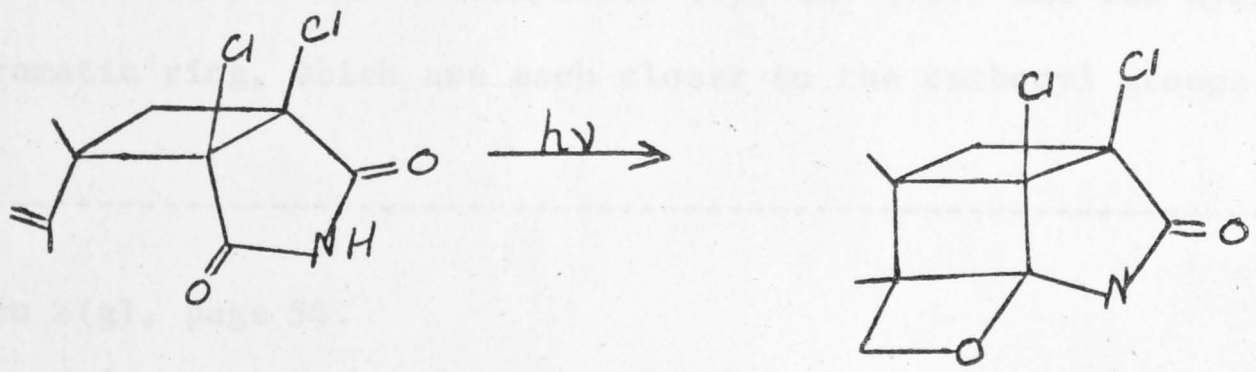
(13)



(15)



(16)



(178)

(177)

and hinders the formation of an oxime at the carbonyl in the 1-position. When (1) is dimerised the methyl group, in each half of the dimer, moves to the trans-configuration, out of the plane of quinonoid ring. This spatial shift of the methyl groups to the less hindering trans-configuration in the dimer allows the formation of a tetra-oxime. It is further argued that the conditions underwhich the dimer is converted to a tetra-oxime would be sufficient to break the oxygen bridges in (145)and allow tetra-oxime formation.

A similar argument applied to Yutaka Asahi's polarographic studies on the dimer (3) would be that a polarographic reduction which could rupture a carbon to carbon bond could readily rupture a carbon to oxygen bond.

Evidence against the oxetan structure (145) is that heating a solution of (145) in ethanol/hydrochloric acid (1:1 by volume) on a waterbath for about four hours did not result in any change in the ultra-violet spectrum.

Some slight support for the double-oxetan structure (145) comes from a study of the aromatic-group signal in the n.m.r. spectra of 2-methyl-naphtho-1,4-quinone dimer (3), and of the adduct (151)* of 2-butyne, and (1). In the compounds (1), and (151) the two hydrogens, on the aromatic ring, which are each closer to the carbonyl groups in

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* Section 2(g), page 54.

the other ring, are shielded. The two hydrogens, in the aromatic ring, which are further away from the carbonyl groups are not effected. This results in the double multiplet pattern observed for the aromatic ring. In the dimer (3) this pattern is not observed. A single, broad multiplet is seen which can be interpreted by postulating that the influence of one of the carbonyls in each half of the dimer has been removed by formation of any oxygen bridge.

More positive support for the double-oxetan structure (145), should come from an examination of the chromophoric groups, and a comparison of the ultraviolet spectra of (145), and of model compounds. While the absorptivities of chromophoric groups are not purely additive, it would seem that ϵ values of a dimer with four functional carbonyl groups should be quite different from the ϵ values of a dimer with only two functional carbonyl groups. The problem was to find suitable model compounds containing only, two carbonyl groups for comparison of the quantitative ultraviolet spectra.

The ϵ values in ethanol of (145) and some model compounds are set out below.

2-methyl-1,4 naphthoquinone dimer (145):

(a) by Zavarin,[4]

λ_{max} = 227 mμ , ϵ = 36,310 ; $\lambda_{I/P}$ = 255 , ϵ = 12,020 ;

λ_{max} = 303 mμ , ϵ = 2,344 ; $\lambda_{I/P}$ = 340-350 , ϵ = 219-190 .

(b) Present work,

λ_{max} = 227 mμ , ϵ = 33,640 ; $\lambda_{I/P}$ = 258 mμ ; ϵ = 14,610 ;
λ_{max} = 305 mμ , ϵ = 2,677 .

2,3-Epoxy-3-methyl-1,4 naphthoquinone (2) by Zavarin:[4]

λ_{max} = 227 mμ , ϵ = 29,510 ; $\lambda_{I/P}$ = 265 mμ , ϵ = 5,754 ;
λ_{max} = 303 mμ , ϵ = 2,399 ; $\lambda_{I/P}$ = 340 mμ , ϵ = 257 .

3,4-Benz-6,7,8-trimethyl-bicyclo (4,2,0) oct-7-ene-2-5-dione (151):

Present work:

λ_{max} = 227 mμ , ϵ = 30,600 ; λ_{max} = 252 mμ , ϵ = 10,107 ;
λ_{max} = 303 mμ , ϵ = 1,510 .

An inspection of these molar absorptivity values indicates that these compounds have ϵ values of the same order at the respective wavelength maxima, or inflection points.

The following data was abstracted from work reported by Bowyer and Porter[52] on the compounds di-indene monoketone dimer (152), α-truxone (153), and indene diketone dimer (154). These are shown in Diagram 33.

Di-indene monoketone (152) in chloroform:

$\lambda_{I/P}$ = 261 , ϵ = 1,950 ; λ_{max} = 267 , ϵ = 2,630 ;
λ_{max} = 273 , ϵ = 2,951 ; $\lambda_{I/P}$ = 278 , ϵ = 1,738 .

α-Truxone (153) in chloroform:

λ_{max} = 274 , ϵ = 1,995 ; $\lambda_{I/P}$ = 280 , ϵ = 1,905 ;
λ_{max} = 293 , ϵ = 447 .

Indene diketone dimer (154) in ethanol:

$\lambda_{I/P}$ = 261 , ϵ = 1,950 ; λ_{max} = 267 , ϵ = 2,630 ;
λ_{max} = 273 , ϵ = 2,951 ; $\lambda_{I/P}$ = 278 , ϵ = 1,738 .

Molar absorptivity values for 1-tetralone (155); and 1-indanone (156) were abstracted from work reported by Hassner and Cromwell.[53] These data are shown below:

1-Tetralone (155) in methanol:

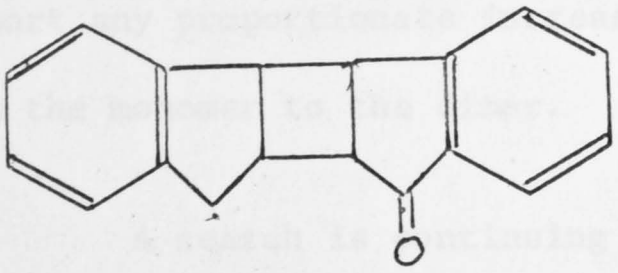
λ_{max} = 248 , ϵ = 11,600 ; λ_{max} = 292 , ϵ = 1,700 .

1-Indanone (156) in acid solution:

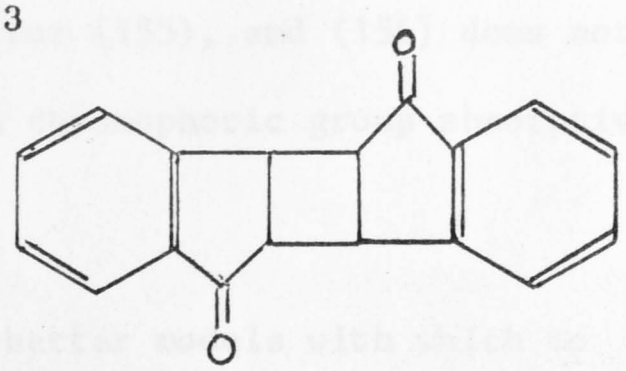
λ_{max} = 243 , ϵ = 12,300 .

With allowance for interaction of chromophoric groups a comparison of the respective absorptivity values for (154), and of those for (155), and (156) supports the two-fold increase of the chromophoric group in (154). On the other hand, a comparison of the absorptivity data for α-truxone (153) with that of di-indene

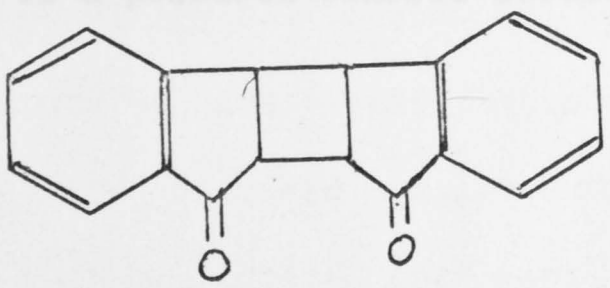
DIAGRAM 33



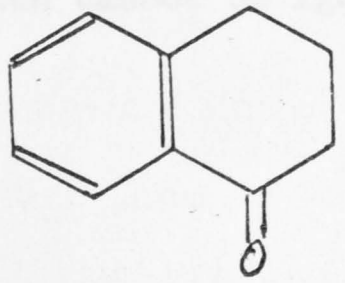
(152)



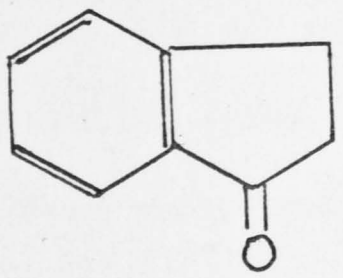
(153)



(154)



(155)



(156)

monoketone (152), and also with that for (155), and (156) does not support any proportionate increase in chromophoric group absorptivity from the monomer to the dimer.

A search is continuing for better models with which to compare the postulated double-oxetan structure (145). While the evidence presented for the existence of the double-oxetan dimer (145) is mainly circumstantial, at least it points the fact that here is a possible dimeric structure which cannot be ignored.

2(g) Other Photo-Cycloaddition Reactions of 2-Methyl 1,4-Naphthoquinone

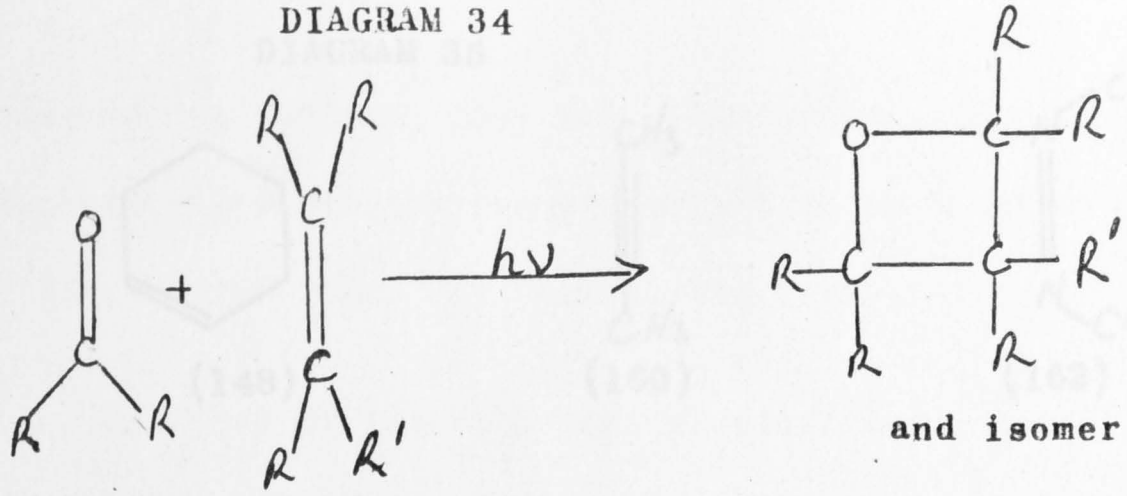
Paterno and Chieffii[54] reported in 1909 that trimethylene oxides, or oxetans, are formed when mixtures of tri-, or tetra-substituted olefines, and aldehydes or ketones are exposed to sunlight, cf. Diagram 34a. Buchi and co-workers[55] in 1954, reinvestigated Paterno's reaction and reported the photochemical addition of acetophenone (157) to 2-methyl-2-butene (158) and recently Bryce-Smith and Gilbert[51] have described the photoaddition of p-quinones to olefines to yield oxetans. Examples are shown in Diagram 34b. They further reported that naphtho-1,4-quinone (146) also gave 1:1 photo adducts with cis-cyclooctene (147).

Zimmerman and Craft,[56] and Gilbert and co-workers[57] have successfully irradiated p-benzoquinone (148) and diphenyl-acetylene (81) to a quinomethide (159), cf. Diagram 34c. In an investigation of the mechanism of photo-cycloaddition of carbonyl compounds, Arnold and co-workers[58] found that the carbonyl n-π^* state is necessary for oxetan formation. Ketones in excited states other than n-π^* are unreactive.

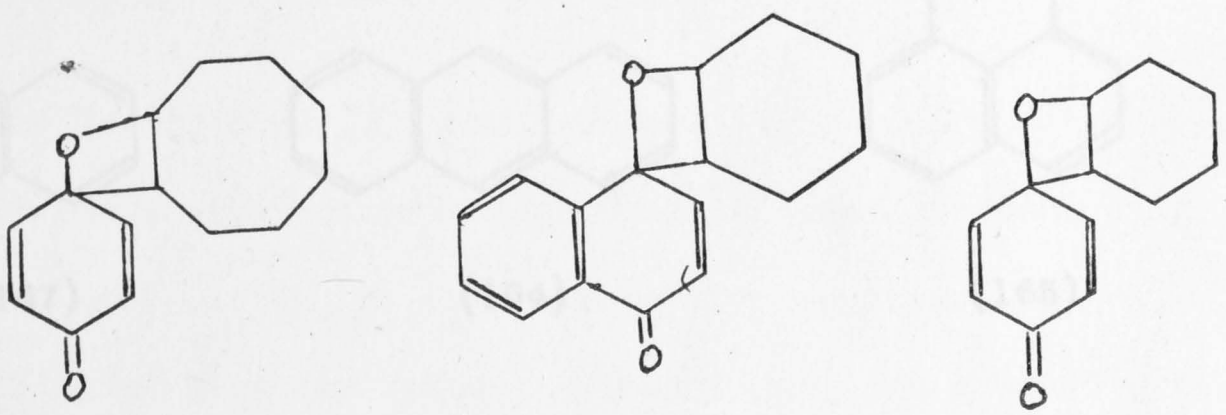
With a view to examining other photo-cycloaddition reactions of 2-methyl-1,4-naphthoquinone (1) than the dimerisation reaction, a series of solutions was set up, each containing the compound (1) (0.0145M), and a compound containing a double, or triple bond system (0.029M). These are shown in Diagram 35.

DIAGRAM 34

(a)



(b)



(c)

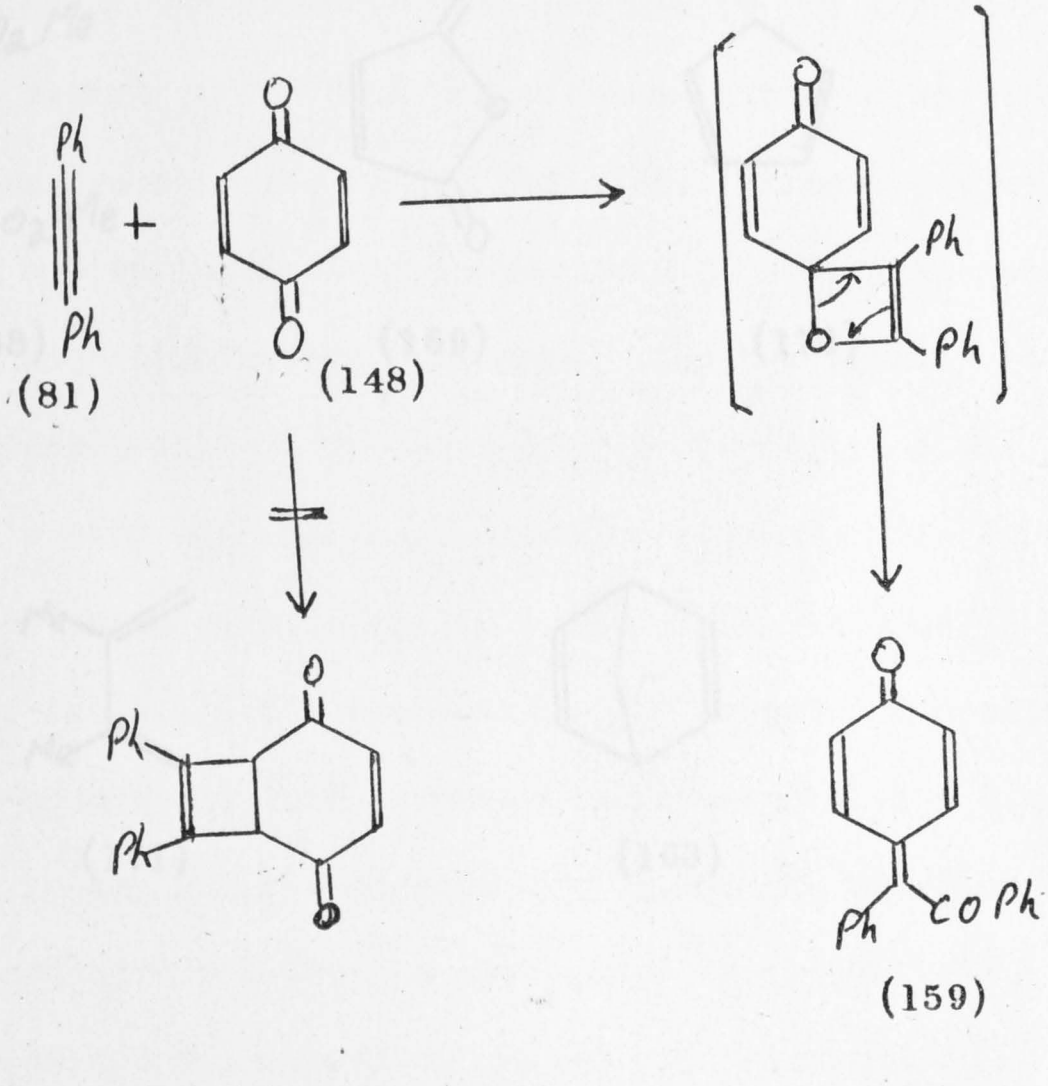
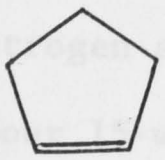


DIAGRAM 35



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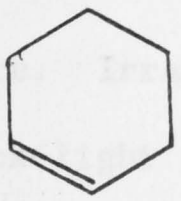
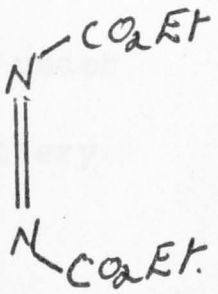
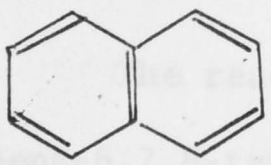


(148)

(160)



(162)



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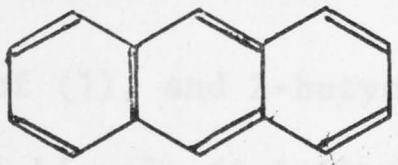

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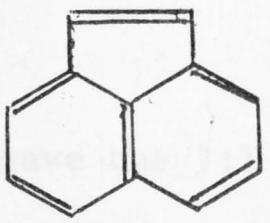

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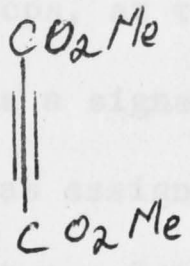

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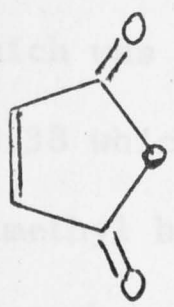
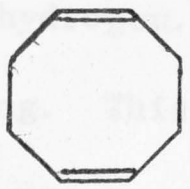
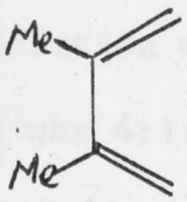


(169)

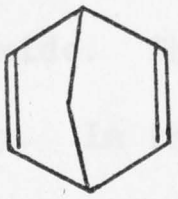
(170)



(172)



(171)



(163)

The solvent was benzene, and each solution was kept under a nitrogen atmosphere. Irradiation was carried out under a battery of four 15-watt black-light tubes for four to six weeks.

To date, only two of the reaction solutions have been examined. These were the reaction of (1), and cyclohexene (148), and the reaction of (1), and 2-butyne (160).

The reaction of (1), and 2-butyne (160) gave the 1:1 adduct, 3,4-benz-6,7,8-trimethyl-bicyclo (4,2,0) oct-7-ene-2,5-dione (151) in 75% yield, analysis ($C_{15}H_{14}O_2$). The n.m.r. spectrum had a double aromatic multiplet over the range $\tau = 2.05 \pm 0.3$, and a broad multiplet over 12 cps, at $\tau = 6.50$, which was assigned to the tertiary hydrogen. There was a signal at $\tau = 8.38$ which showed signs of splitting. This signal was assigned to the methyl hydrogens. Finally, there was a signal at $\tau = 8.48$ which also showed signs of splitting; this was assigned to the vinyl methyl hydrogens. The two signals at $\tau = 8.38$, and $\tau = 8.48$ were together on a base of $\pm$ 9 cps at $\tau = 8.40$. The signal at $\tau = 6.50$ was unchanged after treatment of the deuterated chloroform solution with deuterium oxide. The ratio of the peak integrations was 4:1:3:6 respectively. In the n.m.r. spectrum there was no sign of the vinylic-hydrogen quartet signal at $\tau = 3.16$ which was present in the n.m.r. spectrum of (1), and the vinylic methyl doublet signal at $\tau = 7.82$, had also gone. Heating (151) at 260° for 30 minutes under nitrogen in sealed tube resulted in no change of the n.m.r. spectrum.

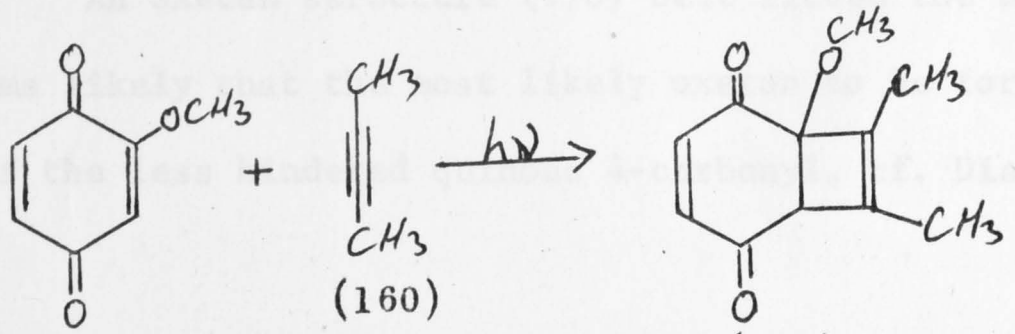
Pappas and Pappas[59] have recently described a cycloaddition in acetonitrile, of 2-methoxy-p-benzo-quinone (173) to 2-butyne (160) to give (174), cf. Diagram 36a. The reported n.m.r. spectrum for (174) had τ = 6.42 (multiplet, broad, methine H), τ = 6.68 (singlet, methoxy H), and τ = 8.3 (complex multiplet, vinyl methyl H). The n.m.r. spectra of (174), and of (151) have similarities and on this basis the cycloaddition product of (1), and 2-butyne (160) was assigned the structure (151).

Pappas and Pappas[59] suggested that the presence of the substituent methoxyl group had a profound effect upon the course of the reaction they described. Other people[60,61] have found that the type of acetylene substituent influences the cause of the cyclo-addition reaction, cf. Diagram 36c.

The other irradiation studied in the series was that of (1), and cyclohexene (148). A golden yellow oil (176) was isolated from this irradiation in 38% yield. An examination of the n.m.r. spectrum showed a double aromatic multiplet over the range τ = 2.1 $\pm$ 0.4, a quartet at τ = 3.17, J = 3 cps assigned to the vinylic hydrogen. A broad multiplet at τ = 7.15 with a base of 14 cps was assigned to methine hydrogen. At τ = 7.80 there was a doublet signal J = 3 cps; this was assigned to the vinyl methyl group. From τ = 8 to τ = 9 there was a complex multiplet pattern which was assigned to the cyclohexene ring methylene groups.

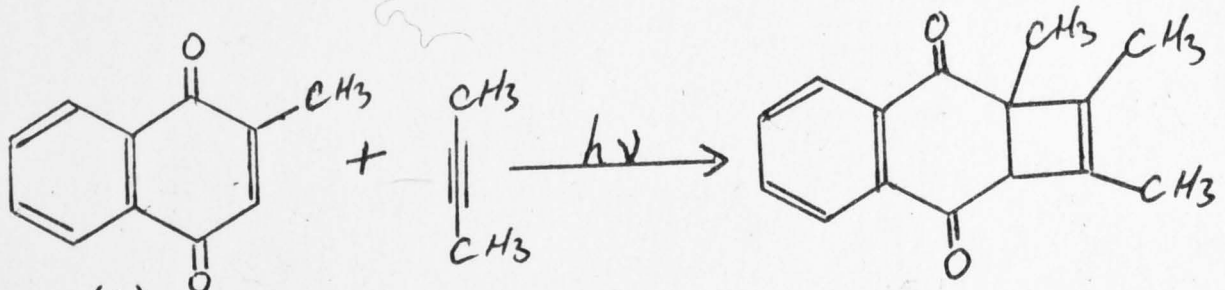
DIAGRAM 36

(a)



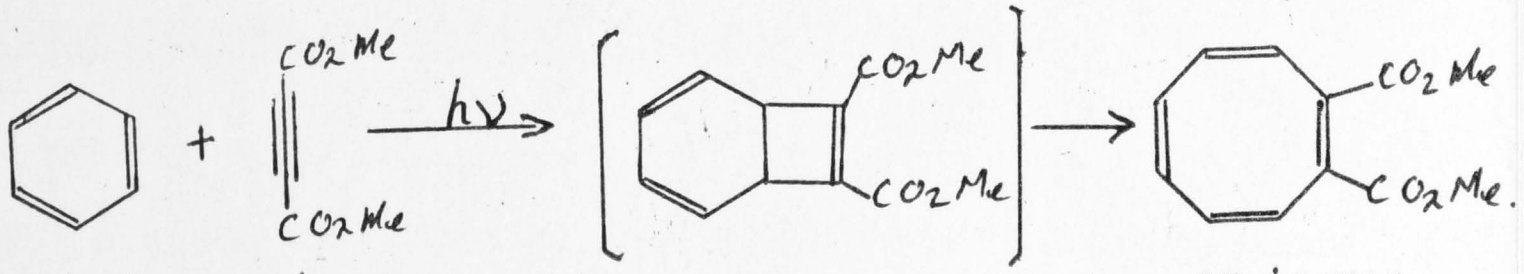
(173) (160) (174)

(b)



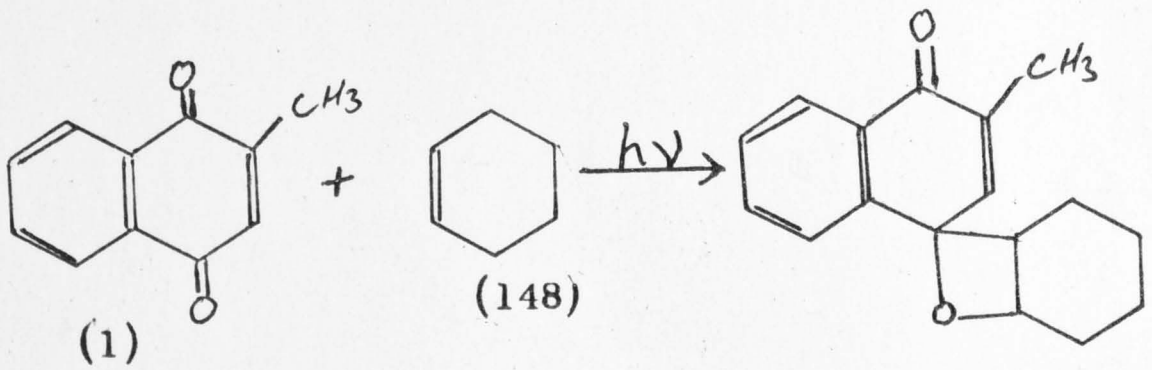
(1) (160) (151)

(c)



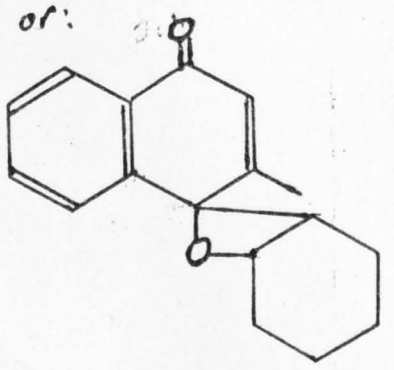
(70) (168) or isomer

(d)



(1) (148) (176)

or:



An oxetan structure (176) best fitted the n.m.r. spectrum. It seems likely that the most likely oxetan to be formed would be that of the less hindered quinone 4-carbonyl, cf. Diagram 36d.

SECTION 3

NUCLEAR MAGNETIC RESONANCE $C^{13}H$ SATELLITE STUDIES

N.m.r. spectroscopy has been useful in elucidating the stereochemistry of thymine (54) and uracil (55) cis-dimers, cf. Diagram 39(a). Anet[20] has determined the coupling constant, $J_{13}\text{-}H_6,H_6$ = = 5 cps, between the identical cyclobutane protons in the C^{12}-H spectrum of the N,N,N',N'-tetramethyl thymine dimer (54). The magnitude of this coupling constant (J = 5 cps) is consistent with vicinal hydrogen atoms, that is, a head to head dimer. The coupling constant does not distinguish between a cis or trans coupling of the hydrogens. This has been determined by workers[65] using other techniques. The method was applied by Blackburn and his co-workers[66] to the 5-deutero-uracil photodimer (55), and gave results similar to those for thymine dimer (54). The $J_{13}\text{-}H_6,H_{6'}$ coupling constant was found to be about 5 cps. The C^{13}H satellite method has also been applied to the photodimers of piperitone(189) by Ziffer and co-workers[67] and led to the conclusion that the dimers were cyclobutane derivatives formed by head to head combinations. The coupling constant $J_{13}H_6\text{-}H_{6'}$ was found to be 7.6 ± 0.2 cps.

In the examples in the literature where the C^{13}H satellite technique has been applied it was stated that it was only possible to differentiate between 1,2 and 1,3 dimeric structures. This was based on the observation by Georgian and co-workers[68] that in the model compound (190) shown in Diagram 39(a), J cis-vicinal ≈ J trans-vicinal.

It is known that cyclobutanes are capable of undergoing conformational change, due to the puckering of the cyclobutane ring.

Where such conformational flexibility exists, the relative position of the vicinal hydrogens changes, and depending on the rate of con formational inversion, this should result in an averaging of the J cis-vicinal couplings. A similar argument can be applied to the J trans-vicinal couplings. An inspection of molecular models of certain of the photodimers indicates that in these cases the dimers are quite rigid due to the 6:4:6 ring fusions. One of the objectives of the project of assigning a configuration to the dimer (3) of 2-methyl naphthoquinone, was to synthesise a number of suitable rigid cyclobutane-containing systems in order to check whether the J cis-vicinal and J trans-vicinal couplings were observably different.

A brief description of the selected model compounds follows. Thymoquinone dimer (8) was prepared according to the method of Liebermann and Ilinski,[69] after preparation of thymoquinone (183) according to the method of Kremers and his co-workers.[63] The dimer (8) had an n.m.r. spectrum with τ = 3.29 (2H, apparent singlet, $W_{\frac{1}{2}}$ = 4 cps, vinyl H), τ = 6.68 (2H, singlet, $W_{\frac{1}{2}}$ = 2-3 cps, cyclobutyl H), τ = 6.95 (2H, quartet, J = 8 cps, methine H) and τ = 9.85 (6H, doublet, J = 8 cps, methyl H). The down field part of the doublet signal coincides with the methyl signal of $\tau \approx$ 8.8 (3H, singlet, methyl H).

The photodimer (191) of citraconic anhydride (34) was prepared according to the method described by Schenck and co-workers.[70] It had an n.m.r. spectrum of τ = 6.84 (2H, apparent singlet, $W_{\frac{1}{2}}$ = 2 cps, cyclobutyl H), and τ = 8.10 (6H, singlet, methyl H).

The adduct (37) of acenaphthylene (19) and duroquinone (36) was prepared according to the method described by Schenck and co-workers.[12] Its n.m.r. spectrum had τ = 6.66 (6H, multiplet, base = 30 cps, aromatic H), τ = 8.33 (4H, singlet, methyl H), and τ = 9.01 (6H, singlet, methyl H).

The adduct* of phenanthrene (192) and dimethyl maleic anhydride (44) had an n.m.r. spectrum of τ = 2.03 (2H, multiplet, base = 18 cps, aromatic H), τ = 2.78 (6H, multiplet, base = 35 cps, aromatic H), τ = 5.79 (2H, apparent singlet, $W_{\frac{1}{2}}$ = 2-3 cps, cyclobutyl H), and τ = 9.12 (6H, singlet, methyl H).

The dimer (193)* of the 4-methyl-coumarin (194) had an n.m.r. spectrum of τ = 2.75 (8H, multiplet, base = 30 cps, aromatic H), τ = 8.58 (2H, apparent singlet, $W_{\frac{1}{2}}$ = 2 cps, cyclobutyl H), and τ = 6.71 (6H, singlet, methyl H). Width at half height $W_{\frac{1}{2}}$ is with respect to trimethylsilane $W_{\frac{1}{2}}$ = 2 cps.

The adduct (195)* of (192) and citraconic anhydride (34) had an n.m.r. spectrum of τ = 2.05 (2H, multiplet, base = 18 cps), τ = 2.8 (6H, multiplet, base = 35 cps, aromatic H), τ = 5.82 (2H, multiplet, $W_{\frac{1}{2}}$ = 6 cps, cyclobutyl H), τ = 6.86 (1H, doublet, J = 2-3 cps,

---

* Supplied by Dr. R. N. Warrener of this Department.

cyclobutyl H), and τ = 8.99 (3H, singlet, methyl H). Width at half height $W_{\frac{1}{2}}$ is with respect to trimethylsilane $W_{\frac{1}{2}}$ = 2 cps.

This last compound is of special interest since it is asymmetric and could allow determination of J cis/trans couplings in an ordinary C^{12}-H n.m.r. spectrum without recourse to $C^{13}H$ satellite study.[81] These model compounds are shown in Figure 39(b). The dimer (3) of 2-methyl-1,4-naphthoquinone (1) was also prepared. Its n.m.r. spectrum had τ = 2.36 (10H, multiplet, base = 30 cps, aromatic H), τ = 6.16 (2H, singlet, W = 2 cps, tertiary H), and τ = 8.40 (6H, singlet, methyl H). Width at half height $W_{\frac{1}{2}}$ is with respect to trimethylsilane, $W_{\frac{1}{2}}$ = 2 cps.

The $C^{13}H$ satellite n.m.r. spectroscopic studies of these model compounds are being carried out in collaboration with Dr. T. Batterham.* No definite assignments can yet be made to the stereochemistry of the cyclobutane ring systems of the model compounds. However, preliminary examination of the 2-methyl-1,4-naphthoquinone dimer (3) has shown a singlet $C^{13}H$ signal at about 60 cps (J_{13} = 120 cps between $C^{13}H$ signals) from the main $C^{12}H$ singlet signal. This singlet signal is consistent with a 1,3 positioning of the tertiary hydrogens and consequently of the two methyl groups.

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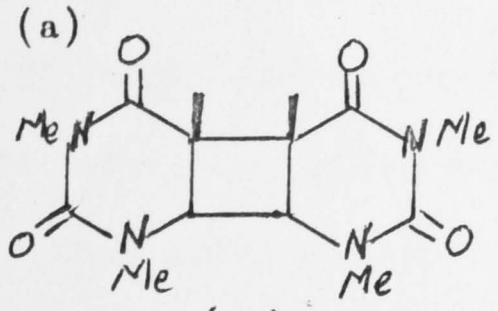
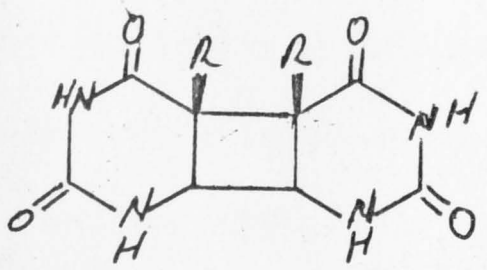
* John Curtin School of Medical Research.

DIAGRAM 39

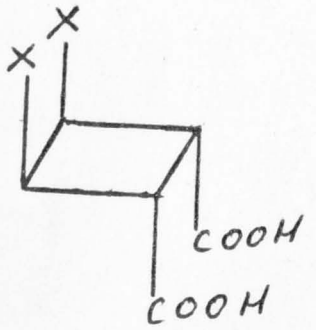
(a)



(54)



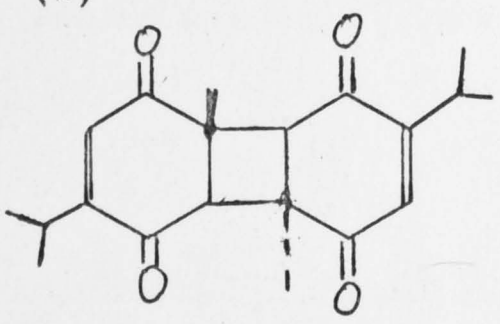
(55)
R = H or D.



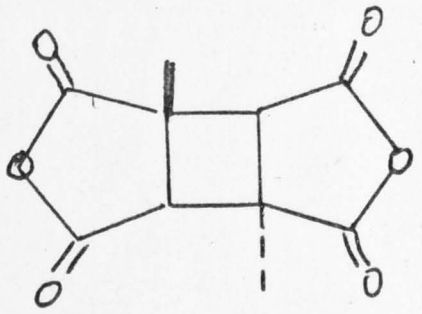
X = Cl, or Br.

(190)

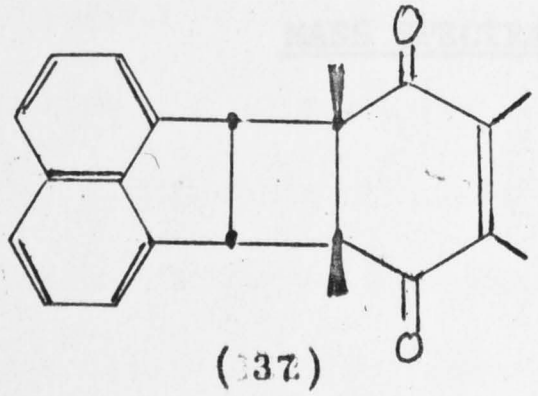
(b)



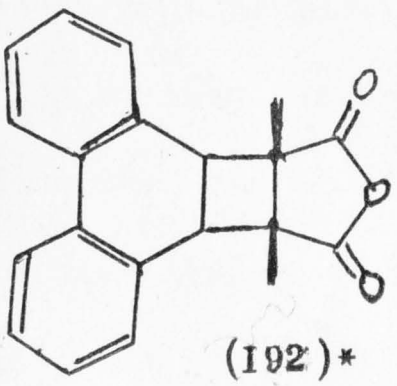
(8)



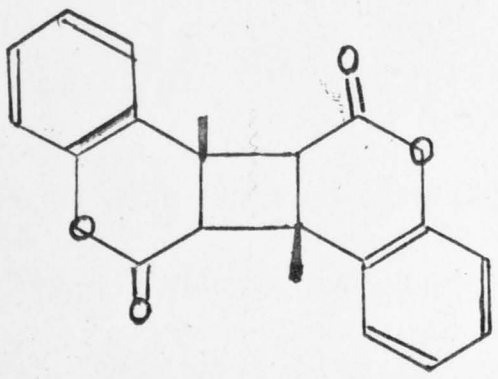
(191)



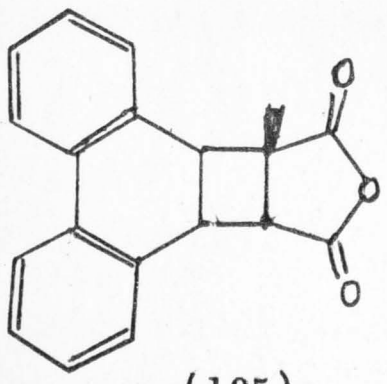
(137)



(192)*



(193)*



(195)*

* and other isomers

SECTION 4

MASS SPECTRAL STUDIES

There have been a number of isolated references to the behaviour of cyclic imides under electron impact, but no systematic study of this group of compounds has yet appeared. As a number of cyclic imides had been prepared, and in view of the interest in the excited state reactions of cyclic anhydrides and imides, a more comprehensive investigation of the effect of electron impact on the cyclic imides was undertaken. These results can be classified as follows.

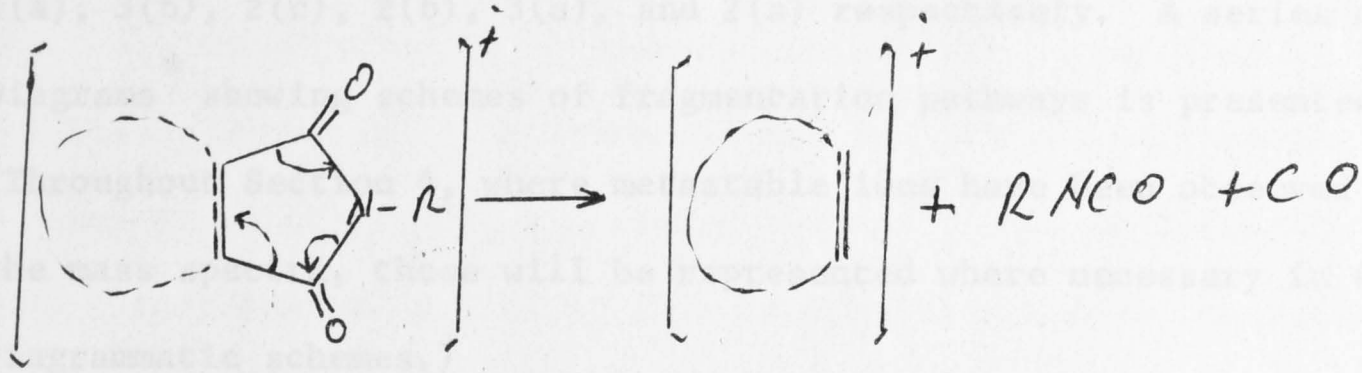
1. Fragmentation of the imide.

This reaction which can be schematically represented as shown in Diagram 40(a) has been observed to occur either as a single concerted step, or as a successive stepwise elimination of the isocyanate, followed by elimination of carbon monoxide, or the reverse. The reaction is particularly favourable with the unsubstituted imides. For example maleimide (196) produces the acetylene ion, m/e 28, 19.8%, Σ_{25} (Table 1, column 1). The other substituted imides studies also showed this reaction to give the acetylene ion (71) in amounts varying from 10.3%, Σ_{25} to 0.68%, Σ_{25}. (Table 1, column 1.)

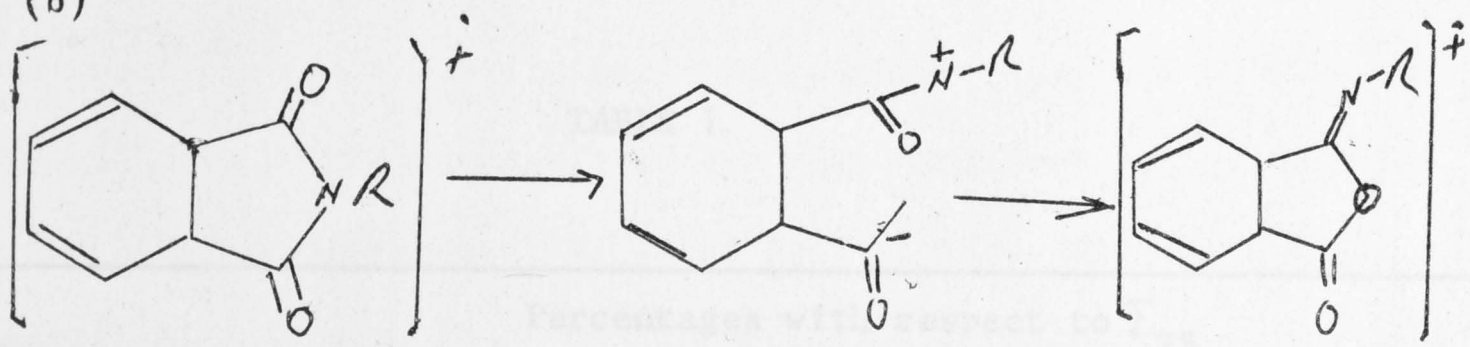
The cyclic imides studied were maleimide (196), N-ethyl maleimide (197), N-benzyl maleimide (84), N-phenyl maleimide (198), isoimide (199), N-benzyl citraconimide (181), and N-phenyl dimethyl maleimide (200). Table 1 indicates the respective percentages according to Σ_{25} of the main fragments formed in each case. A simplified mass

DIAGRAM 40

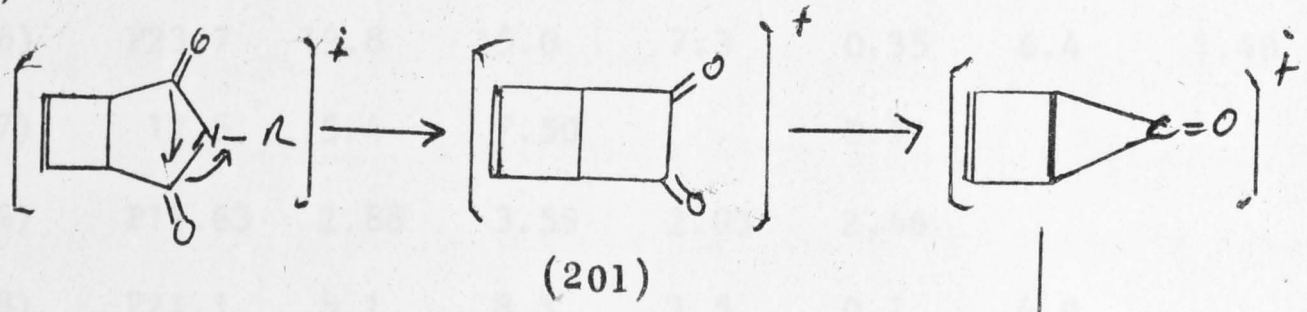
(a)



(b)

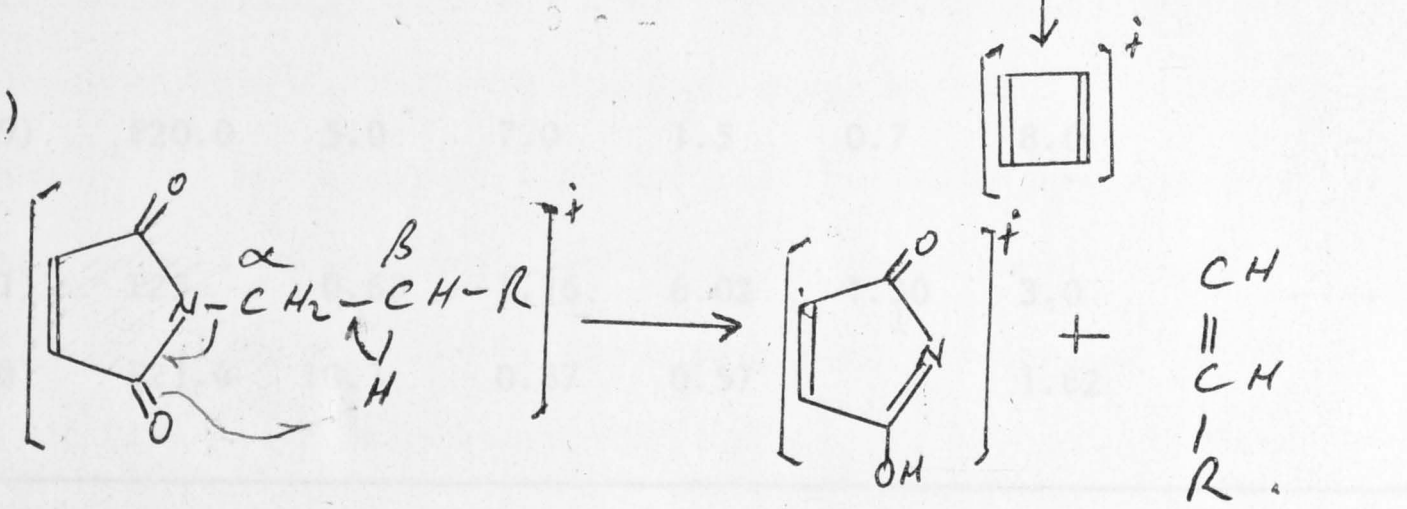


(c)



(201)

(d)



spectrum for each of the above imides is to be found in Figures 1(b), 1(a), 3(b), 2(c), 2(b), 3(a), and 2(a) respectively. A series of Diagrams* showing schemes of fragmentation pathways is presented. (Throughout Section 4, where metastable ions have been observed in the mass spectra, these will be represented where necessary in the Diagrammatic schemes.)

TABLE 1

	Percentages with respect to Σ_{25} *						
Compound	M	1	2	3	4	5	6	7
(196)	P23.7	19.8	15.0	7.3	0.35	6.4	1.40	
(197)	12.6	5.4	7.50		8.1			P23.0
(84)	P11.63	2.88	3.59	2.03	2.46			
(198)	P21.1	5.1	8.5	1.5	0.7	4.9		
(199)	P20.0	5.0	7.0	1.5	0.7	8.0		
(181)	P$\tilde{25}$	0.68	1.16	6.02	1.30	3.0		
(200)	P21.4	10.3	0.87	0.57		1.62		

* The number at the head of each column refers to the fragment eliminated thus: 1 ≡ $-RNC_2O_2$; 2 ≡ -RNCO; 3 ≡ -CO; 4 ≡ -RN; 5 ≡ $-CO_2$; 6 ≡ -RNC; and 7 ≡ $-CH_3$.

---

* Diagrams 41 and 42.

2. Isomerisation/fragmentation.

As observed by Johnson and co-workers,[71] and also by Cotter and his co-workers,[72] the N-substituted phthalimide derivatives (where R = methyl or diphenyl), all showed strong (M-44) ion radicals. These were interpretated as arising from an isomerisation of the imide to a species related more closely to the isoimide, cf. Diagram 40(b). This reaction is not restricted to the phthalimides, but is also observed with the maleimides. It has been confirmed by the reaction of the isomeric isoimide (199) which does in fact, show this ready loss of CO_2. To show that the fragmentation pathway of the substituted imides to the olefine fragments could pass through an initial rearrangement to the isoimide, N-phenyl isomaleimide (199), was prepared by the method of Cotter and his co-workers,[73] was studied. The mass spectrum of (199) was indistinguishable from that of N-phenyl maleimide (198) with regard to the fragmentation pattern, and to the relative intensities of the peaks. Figures 2(b) and 2(c). The corresponding reaction was also observed with di-thiophthalimides, where M-76 (CS_2) peaks were observed.[74] It would appear that not all the imides undergo this rearrangement as judged by the intensity of their (M-44) peaks. As the data in Column 5, Table 1, indicates, this elimination of CO_2 has taken place with maleimide (196) 6.4%, Σ_{25} , N-ethyl maleimide (197) 3.5%, Σ_{25} , N-phenyl maleimide (198) 4.9%, Σ_{25} , but did not occur with N-benzyl maleimide (84) nor with N-benzyl citraconimide

DIAGRAM 41

(a) Maleimide (196)

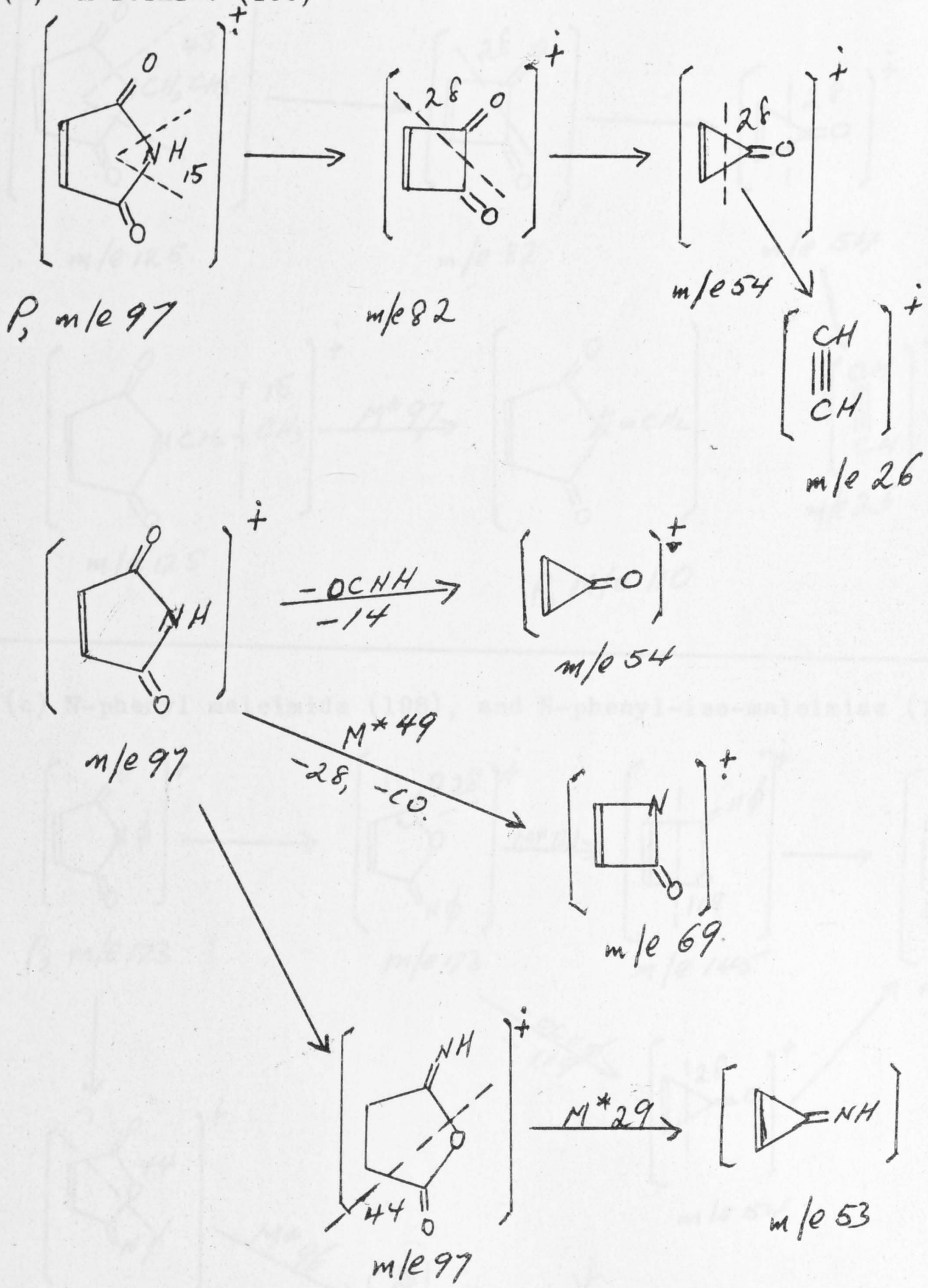
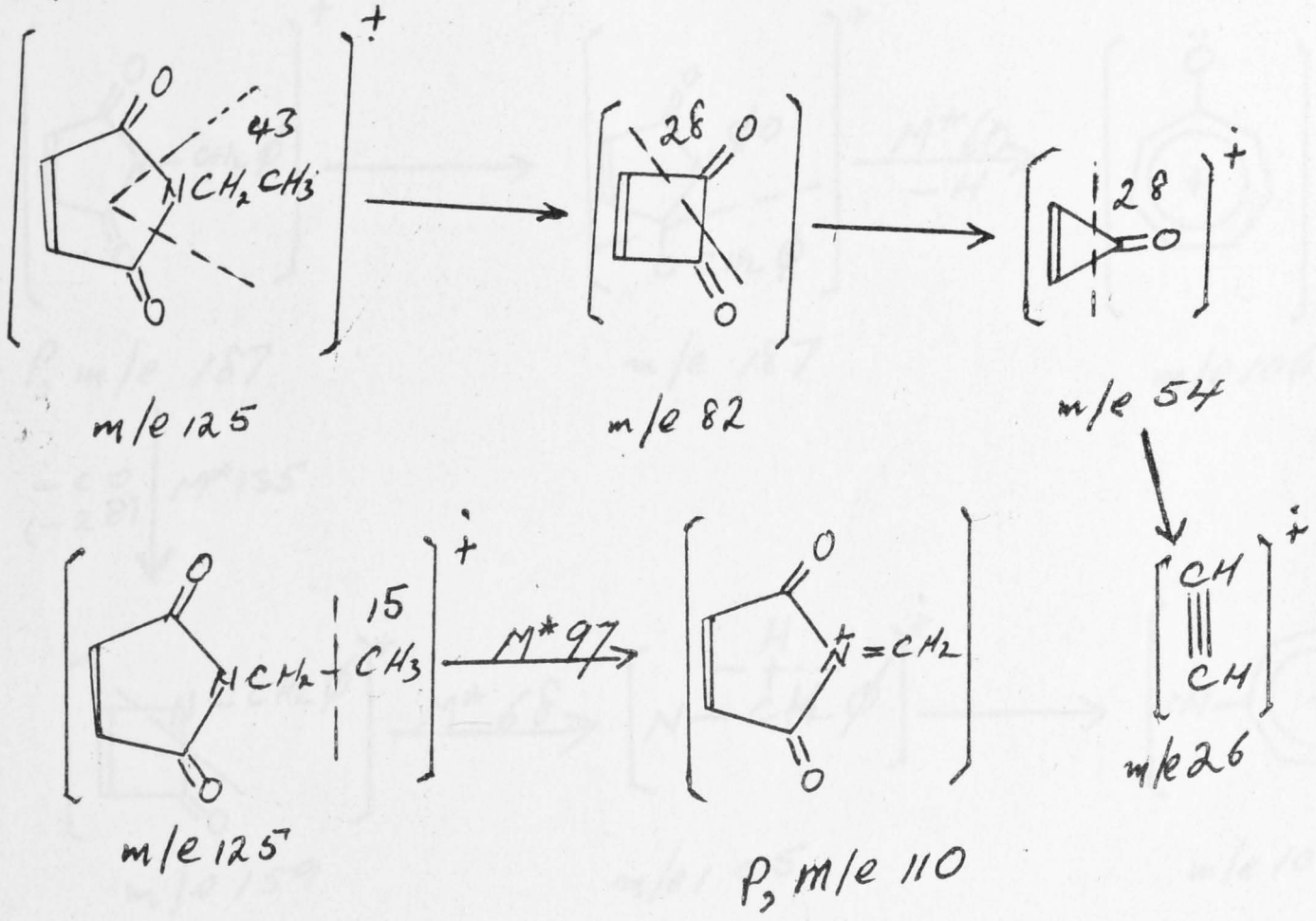


DIAGRAM 41

(b) N-ethyl-maleimide (197)



(c) N-phenyl maleimide (198), and N-phenyl-iso-maleimide (199)

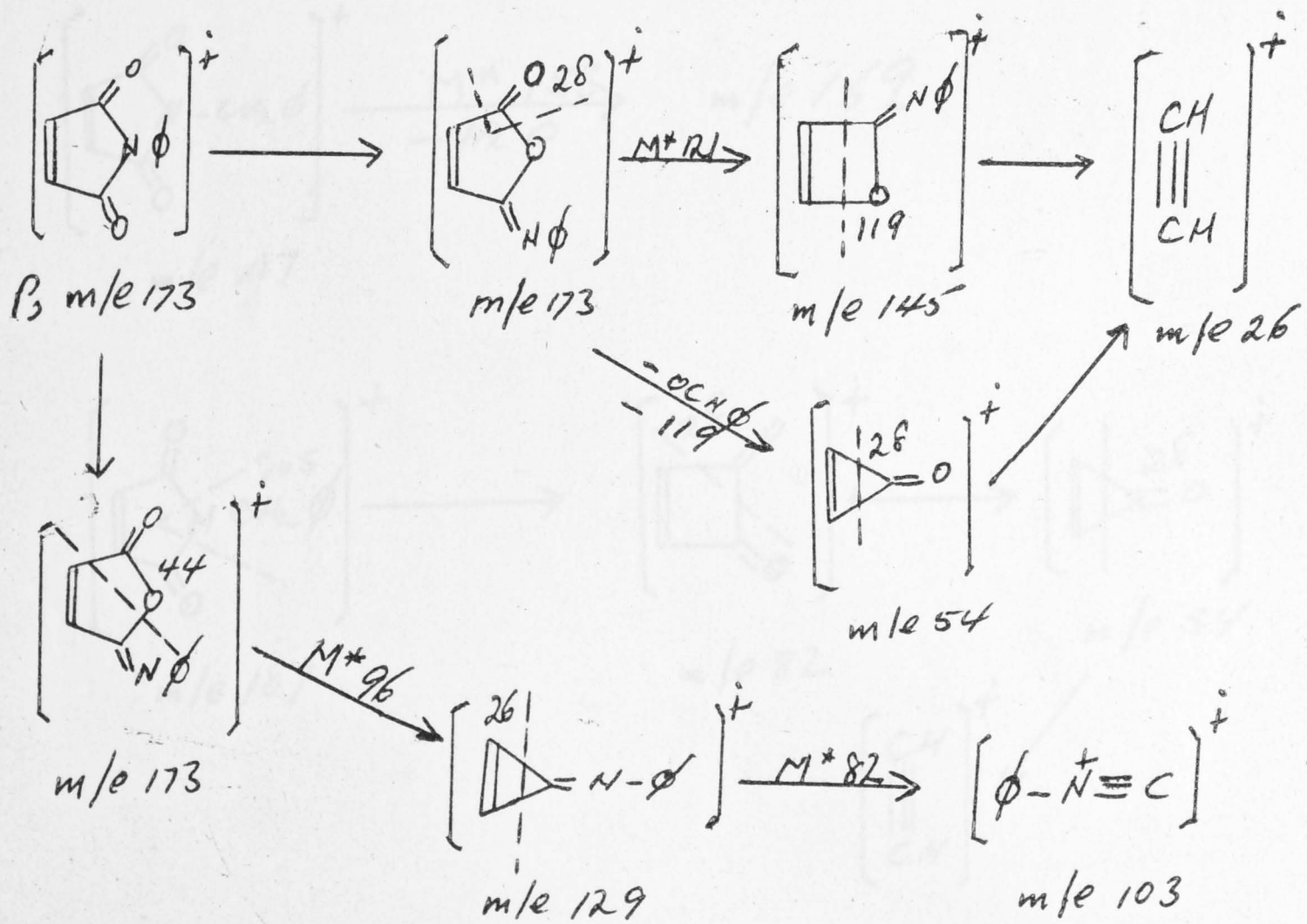
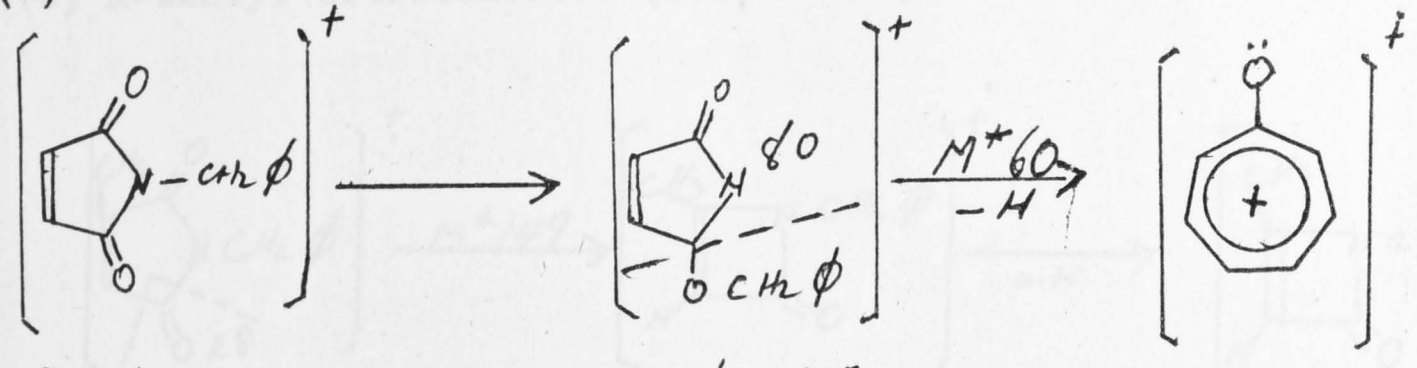


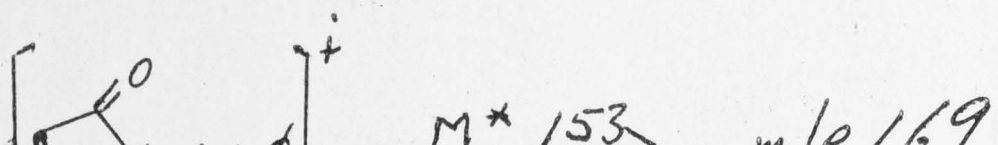
DIAGRAM 42

(a) N-benzyl maleimide (84)

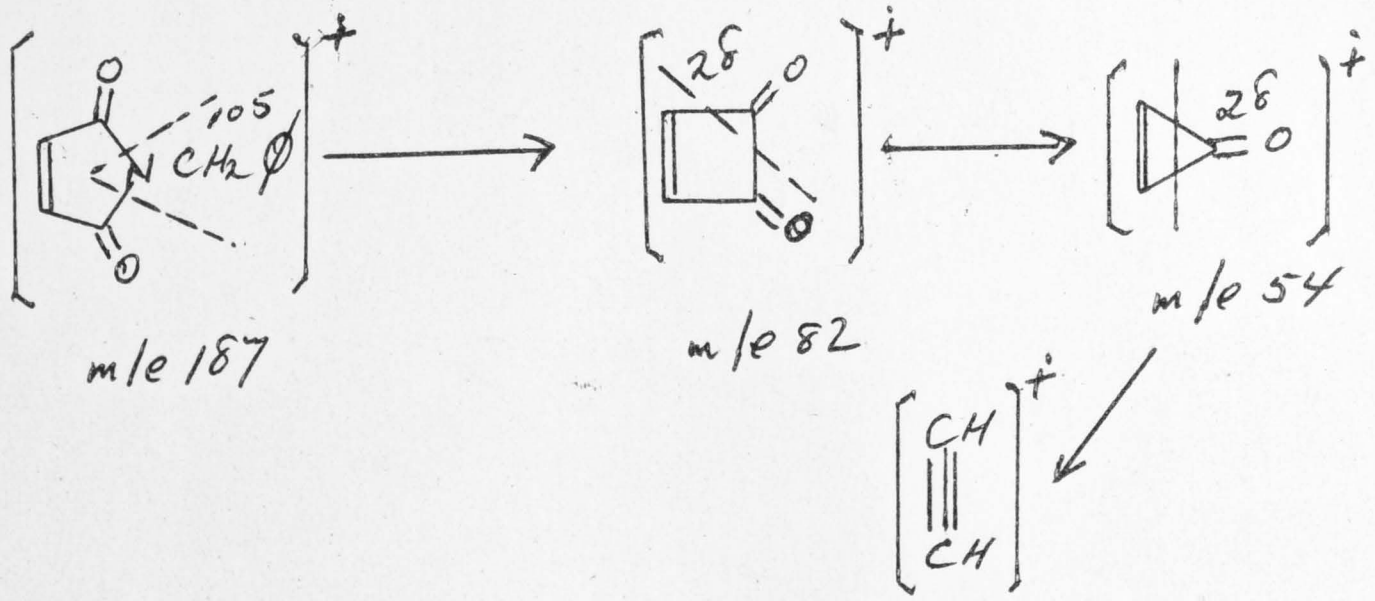


P, m/e 187 — m/e 187 — m/e 106

m/e 159 — m/e 105 — m/e 104



m/e 187 — m/e 169.

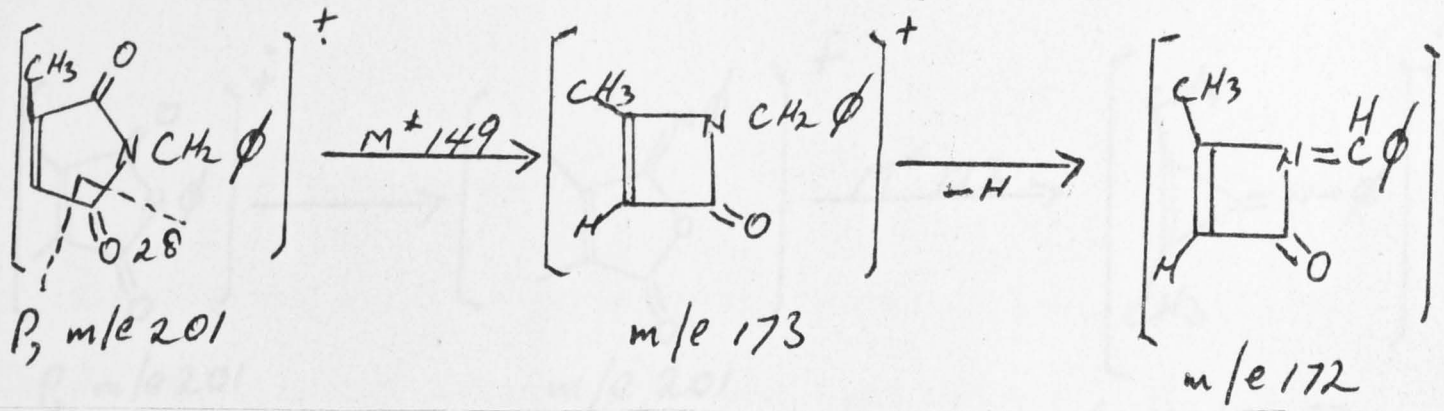


m/e 187 — m/e 82 — m/e 54

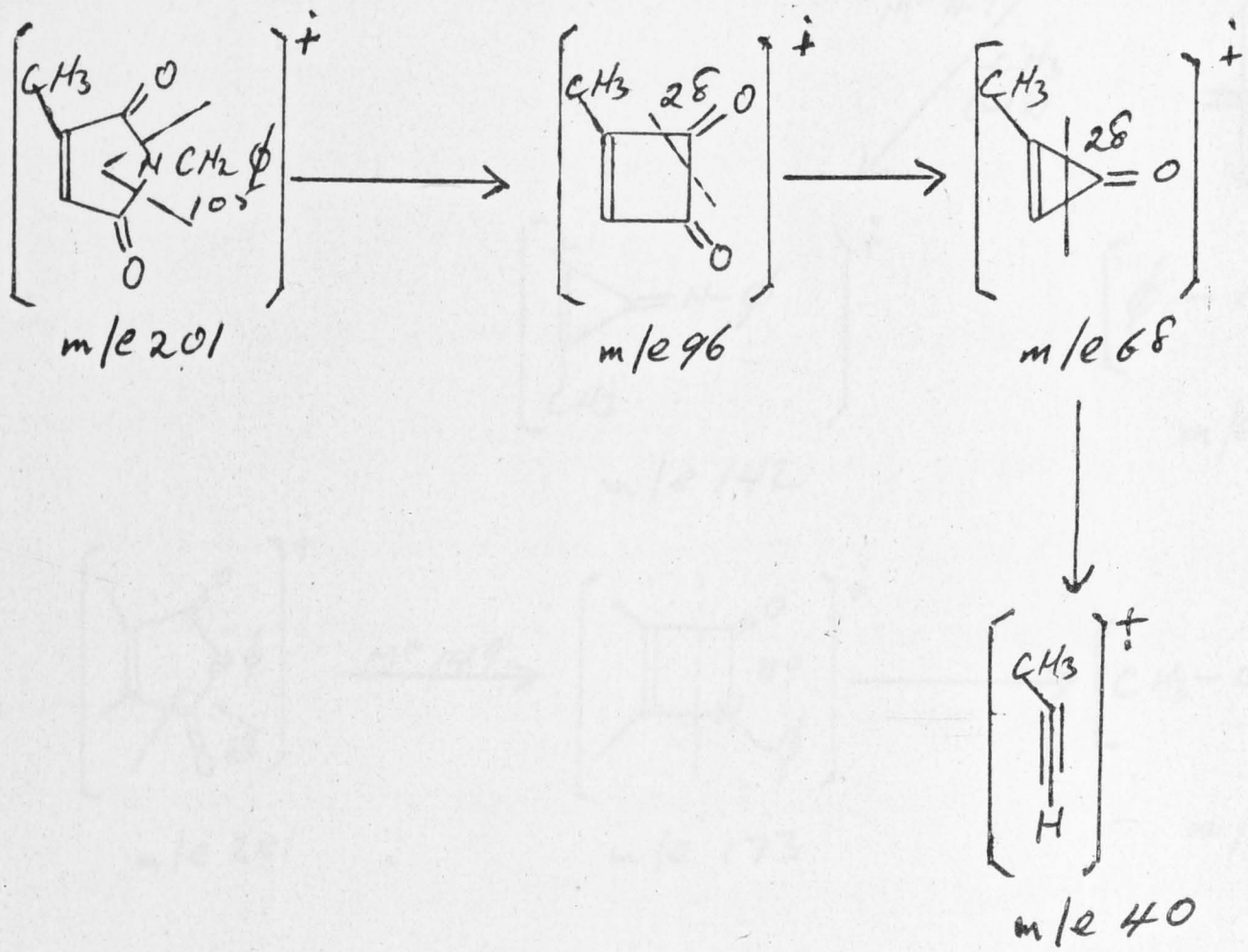
m/e 54 → CH, CH

DIAGRAM 42

(b) N-benzyl citraconimide (181)



P, m/e 201 m/e 173 m/e 172

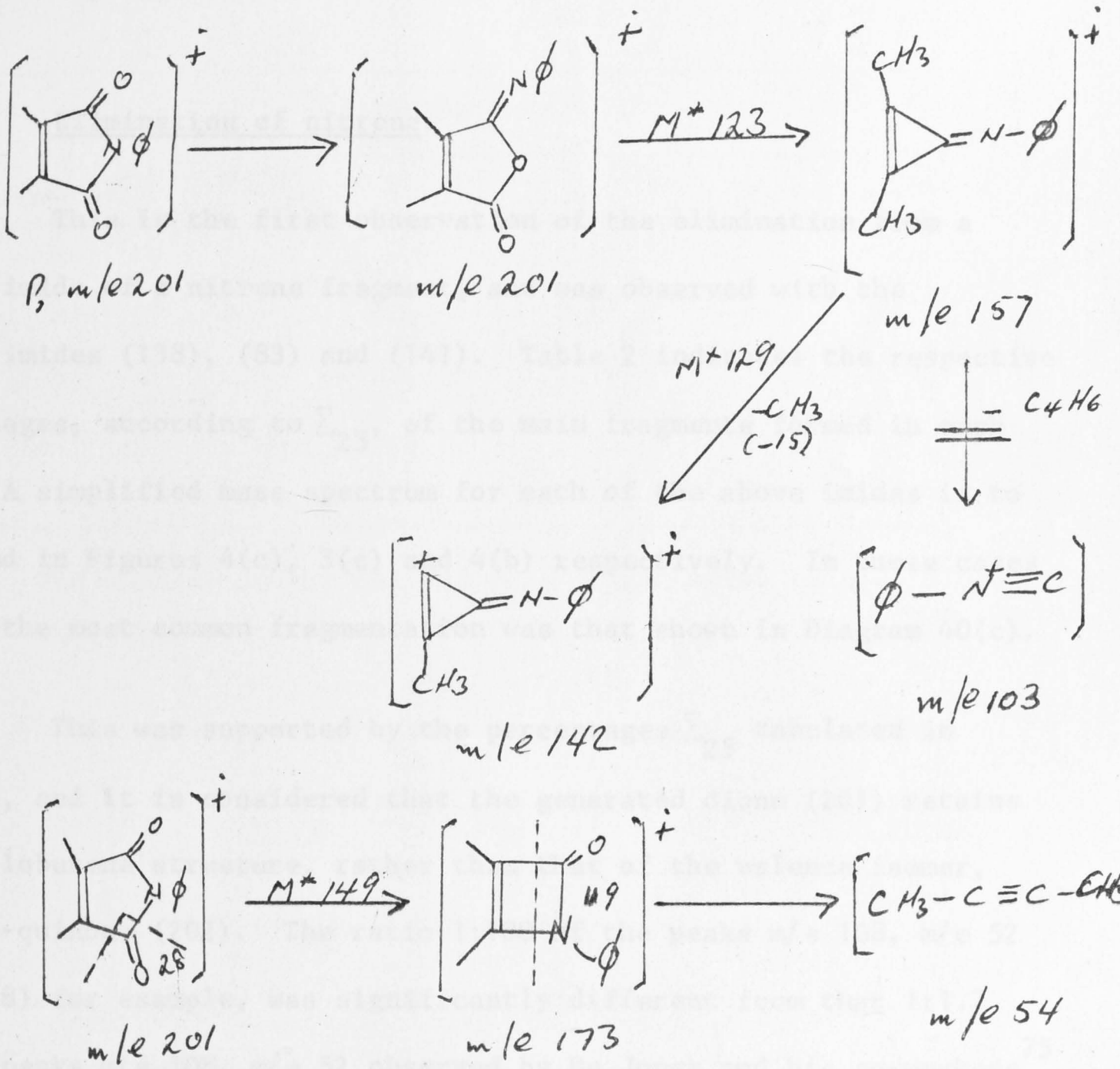


m/e 201 m/e 96 m/e 68

m/e 40

DIAGRAM 42

(c) N-phenyl-dimethylmaleimide (200)



(181). A series of Diagrams* showing schemes of fragmentation pathways is presented.

3. Elimination of nitrene.

This is the first observation of the elimination from a cyclic imide of a nitrene fragment, and was observed with the cyclic imides (138), (83) and (141). Table 2 indicates the respective percentages, according to Σ_{25}, of the main fragments formed in each case. A simplified mass spectrum for each of the above imides is to be found in Figures 4(c), 3(c) and 4(b) respectively. In these cases by far the most common fragmentation was that shown in Diagram 40(c).

This was supported by the percentages Σ_{25} tabulated in Table 2, and it is considered that the generated dione (201) retains the cyclobutene structure, rather than that of the valence isomer, o-benzo-quinone (202). The ratio 1:180 of the peaks m/e 108, m/e 52 for (138) for example, was significantly different from that 1:1.7 of the peaks m/e 108, m/e 52 observed by De Jongh and his co-workers[75] for o-benzo-quinone (203) itself, or when it was generated by fragmentation of phenylene sulphite (204). A series of Diagrams** showing schemes of fragmentation pathways, is presented.

---

* Diagrams 41 and 42.

** Diagram 43.

TABLE 2

Compound	Percentages with respect to Σ_{25} *			
	M	1	2	3	4
(138)	15.6	P24.6	9.47		0.14
(83)	10.4	P18.5	3.78		4.92
(141)	10.0	P29.4	2.60		

* The numbers at the head of each column refer to the fragment eliminated, thus: 1 ≡ $-RNC_2O_2$; 2 ≡ RNCO; 3 ≡ -CO; 4 ≡ -RN.

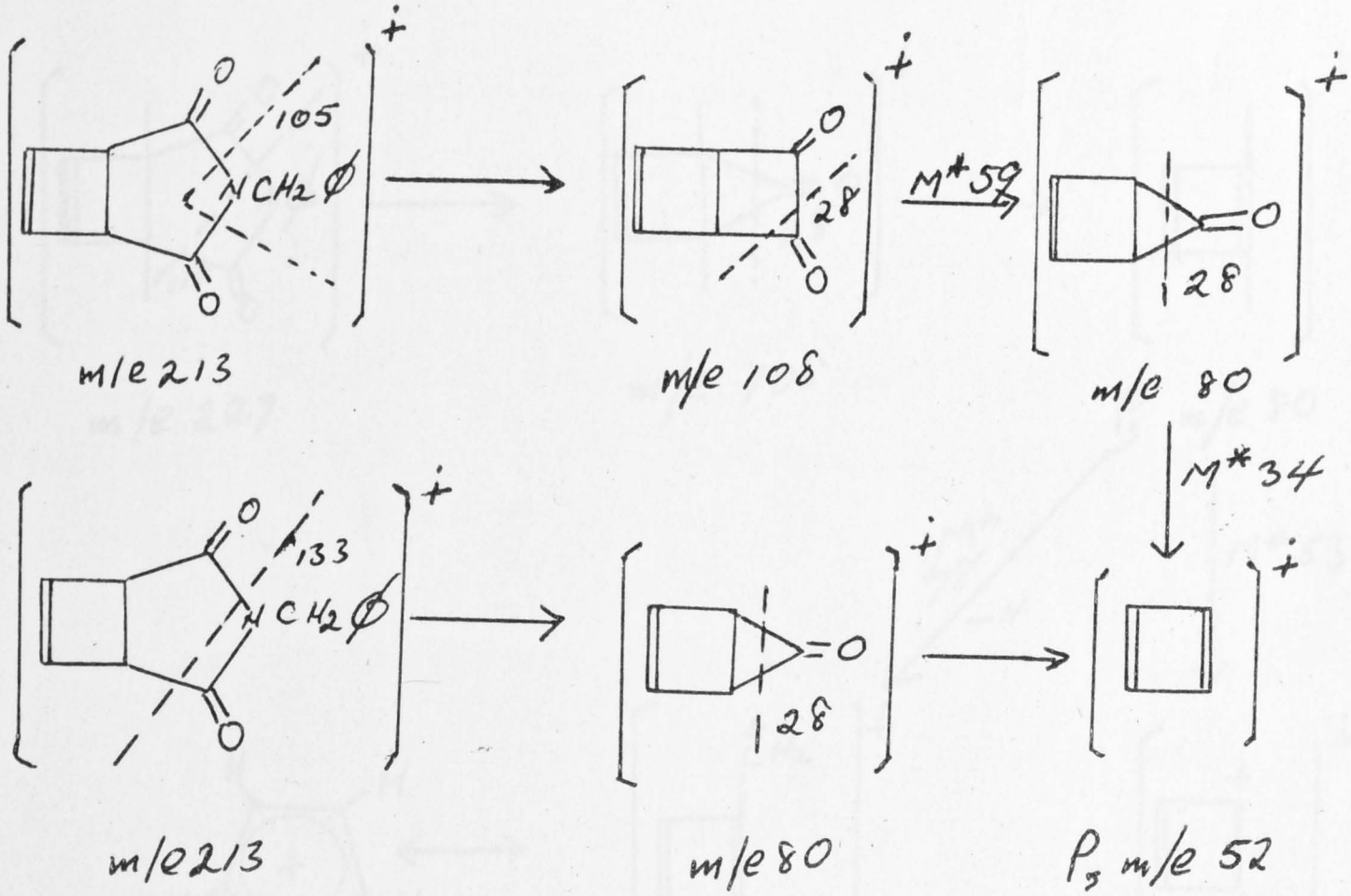
4. Cyclisation of the N-Substituent.

Aplin and co-workers[76] have reported that N-alkyl phthalimides, and N-phthaloylamino-acids showed major peaks in the mass spectrum corresponding to cyclisation of the N-substituent onto the amide carbonyl of the imide.

A similar reaction may have occurred with N-benzyl maleimide (84) m/e 187 as evidenced by the peak m/e 169, 1.5%, Σ_{25} in the mass spectrum shown in Figure 3(b). However, the reaction has yet to be confirmed.

DIAGRAM 43

(a) N-benzyl-cyclobutene-cis-3,4-dicarboximide (83)



(b) N-phenyl-cyclobutene-cis-3,4-dicarboximide (138)

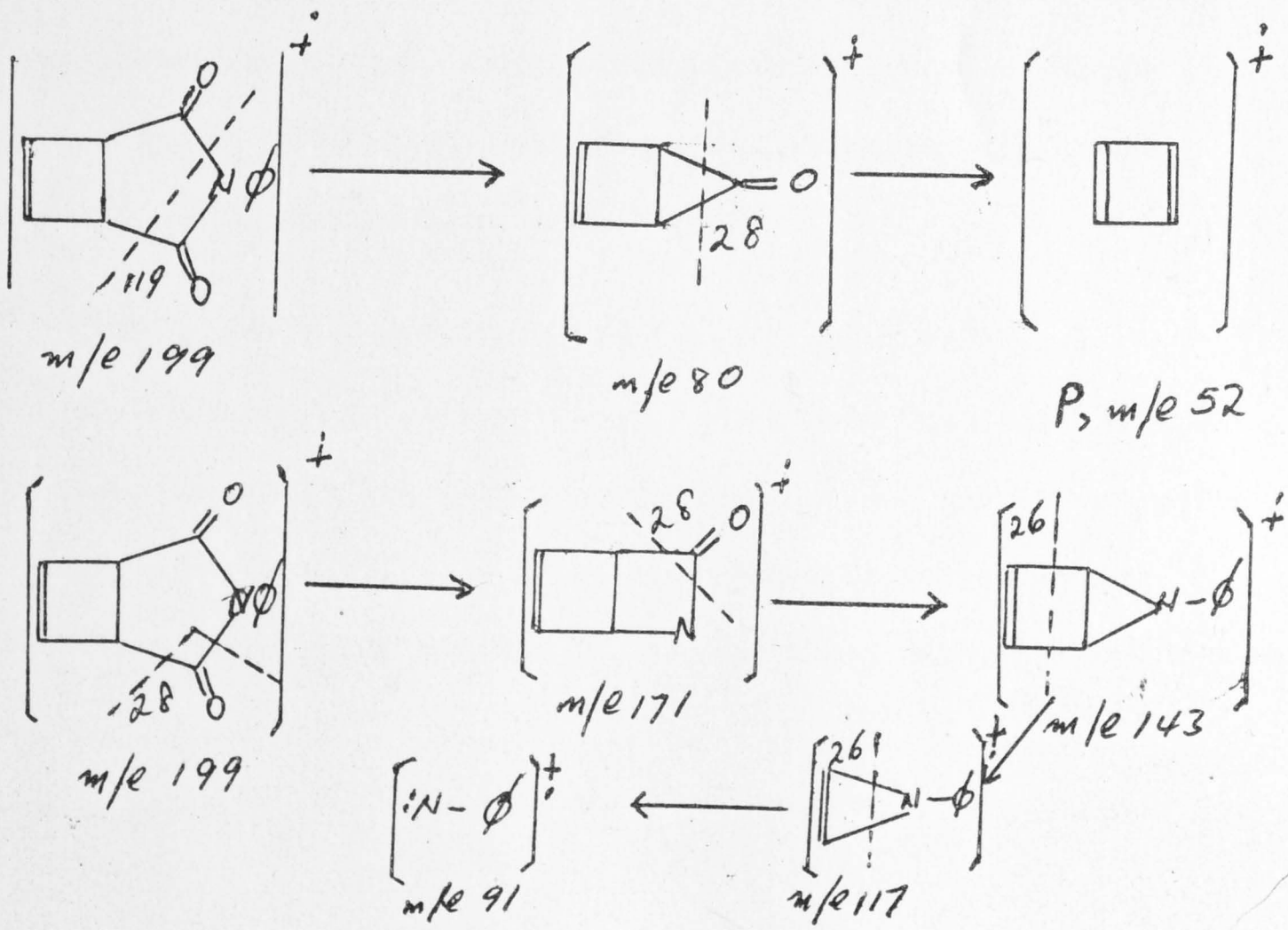
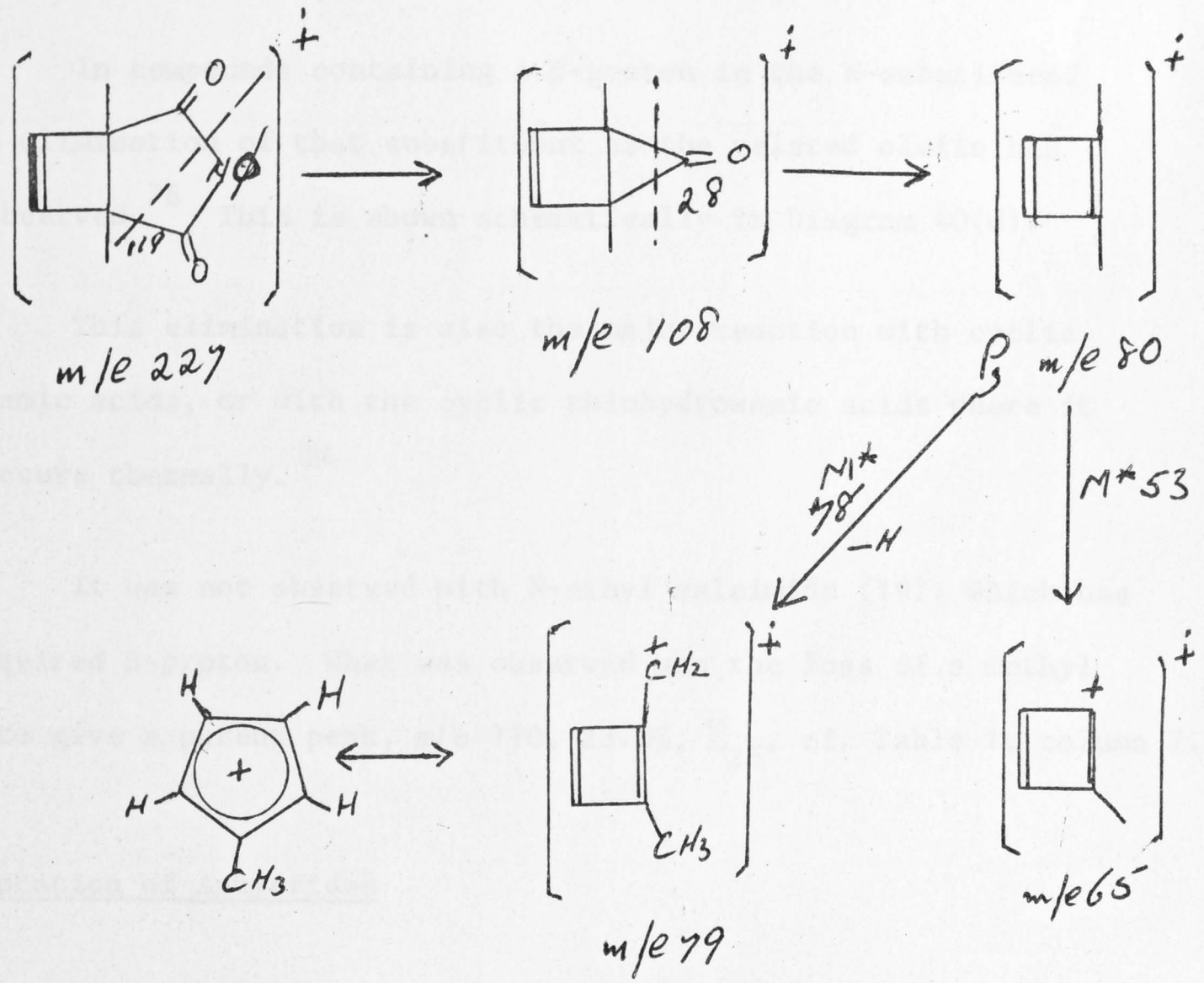


DIAGRAM 43

(c) N-phenyl-3,4-dimethyl-cyclobutene-cis-3,4-dicarboximide (141)



5. Elimination of the N-Substituent Group.

In compounds containing a β-proton in the N-substituent group, elimination of that substituent as the related olefin has been observed.[76] This is shown schematically in Diagram 40(d).

This elimination is also the major reaction with cyclic hydroxamic acids, or with the cyclic thiohydroxamic acids where it also occurs thermally.[74]

It was not observed with N-ethyl maleimide (197) which has the required β-proton. What was observed was the loss of a methyl group to give a parent peak, m/e 110, 23.0%, Σ_{25}, cf. Table 1, column 7.

Fragmentation of Anhydrides

Some anhydrides were also studied, and appeared to fragment in a manner similar to that of the cyclic imides either as single concerted step, or as a successive stepwise elimination of carbon dioxide, and carbon monoxide, or the reverse.

The anhydrides are listed in Table 3 which indicates the respective percentages according to Σ_{25} of the main fragments formed in each case. A simplified mass spectrum for each of the above anhydrides is to be found in Figures 5(b), 5(c), 6(b) and 6(c) respectively. A series of Diagrams* showing schemes of fragmentation pathways is presented.

---

* Diagram 44.

TABLE 3

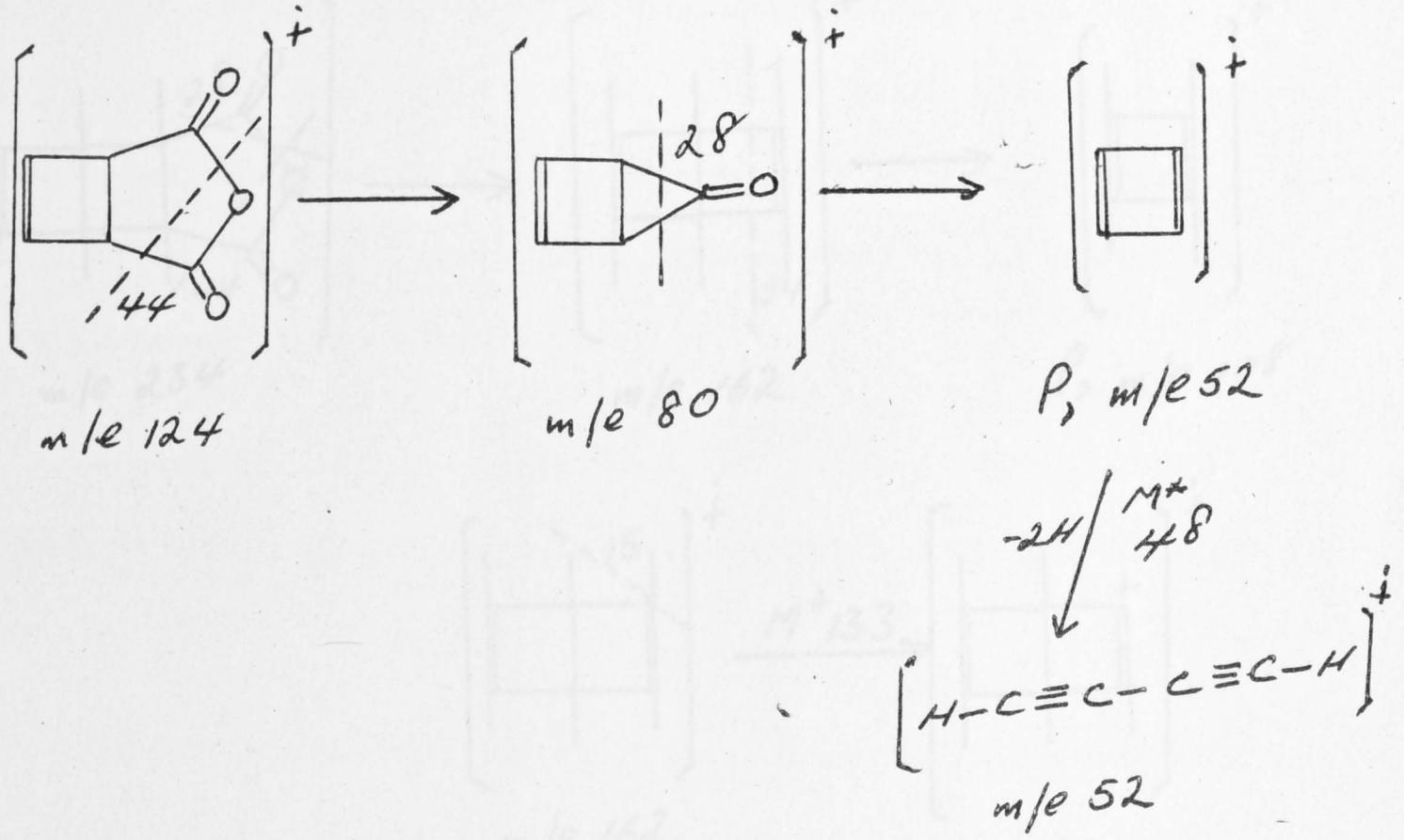
Compound	Percentages with respect to Σ_{25} *					
	M	1	2	3	4	5	6
(89)	0.16	P41.0	8.15				
(91)		P28.0	1.47				
(205)	1.52	8.30		2.6		P11.2	8.5
(56)	2.0	16.52				P23.55	

* The numbers at the head of each column refer to the fragment eliminated, thus: $1 \equiv -C_2O_3$; $2 \equiv -CO_2$; $3 \equiv -CO$; $4 \equiv -O$.

The anhydrides (89) and (91) both have simple mass spectra and appeared to fragment to the cyclobutadiene ion. In both instances this latter fragment corresponded to the parent peak and is considered to retain its cyclobutadiene character. In support of this, Corey and Streith[77] have observed the mass spectral fragmentation of the photoisomer (206) of 2-pyrone, and of the photoisomer (207) of N-methyl 2-pyridone to give a cyclobutadiene ion. Beynon and his co-workers[78] have described the fragmentation of tetracyclone to give as a major reaction product the tetraphenylcyclobutadiene ion.

DIAGRAM 44

(a) Cyclobutene-<u>cis</u>-3,4-dicarboxylic anhydride (89)



(b) 3,4-dimethyl-cyclobutene-<u>cis</u>-3,4-dicarboxylic anhydride (91)

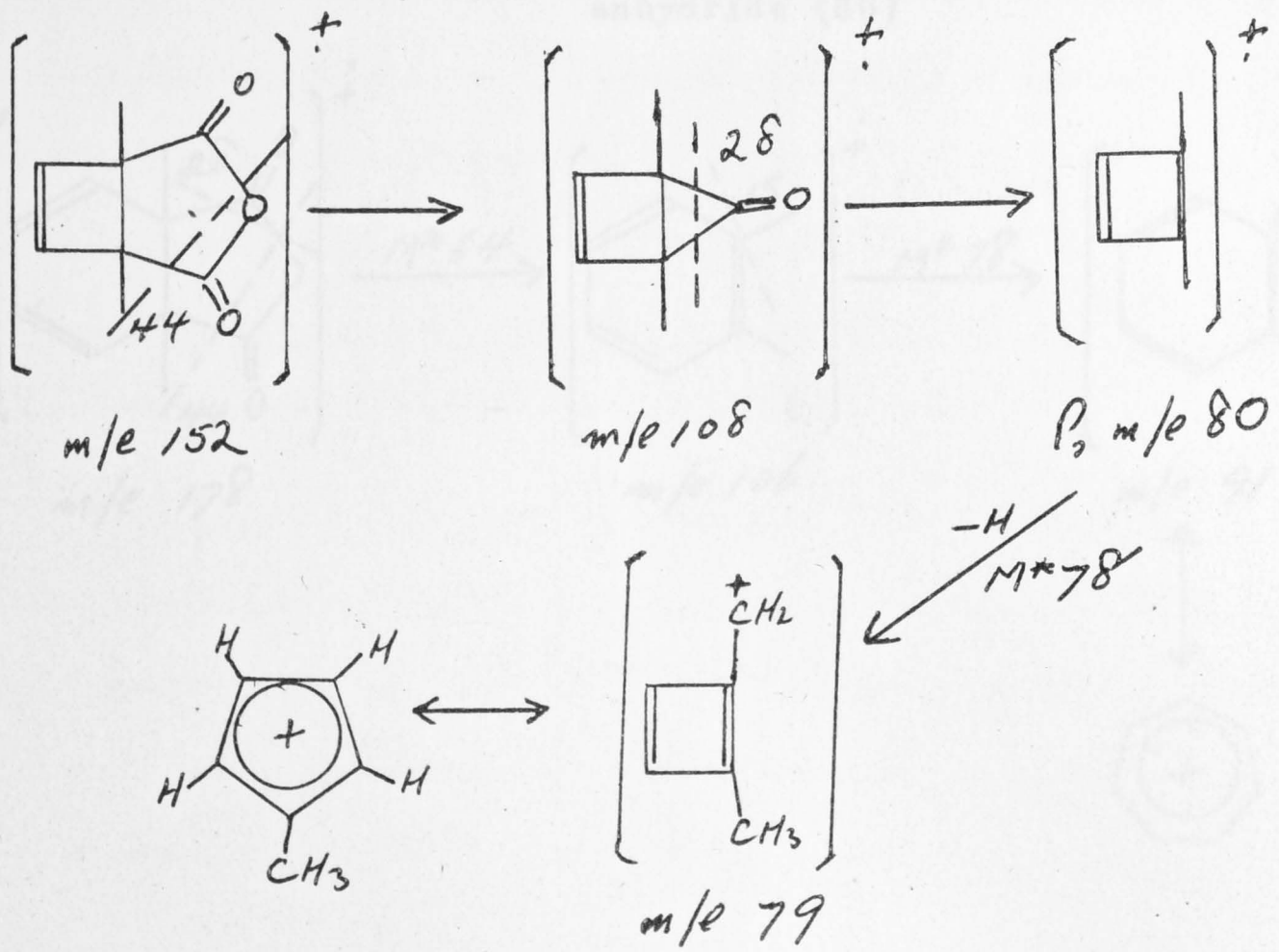
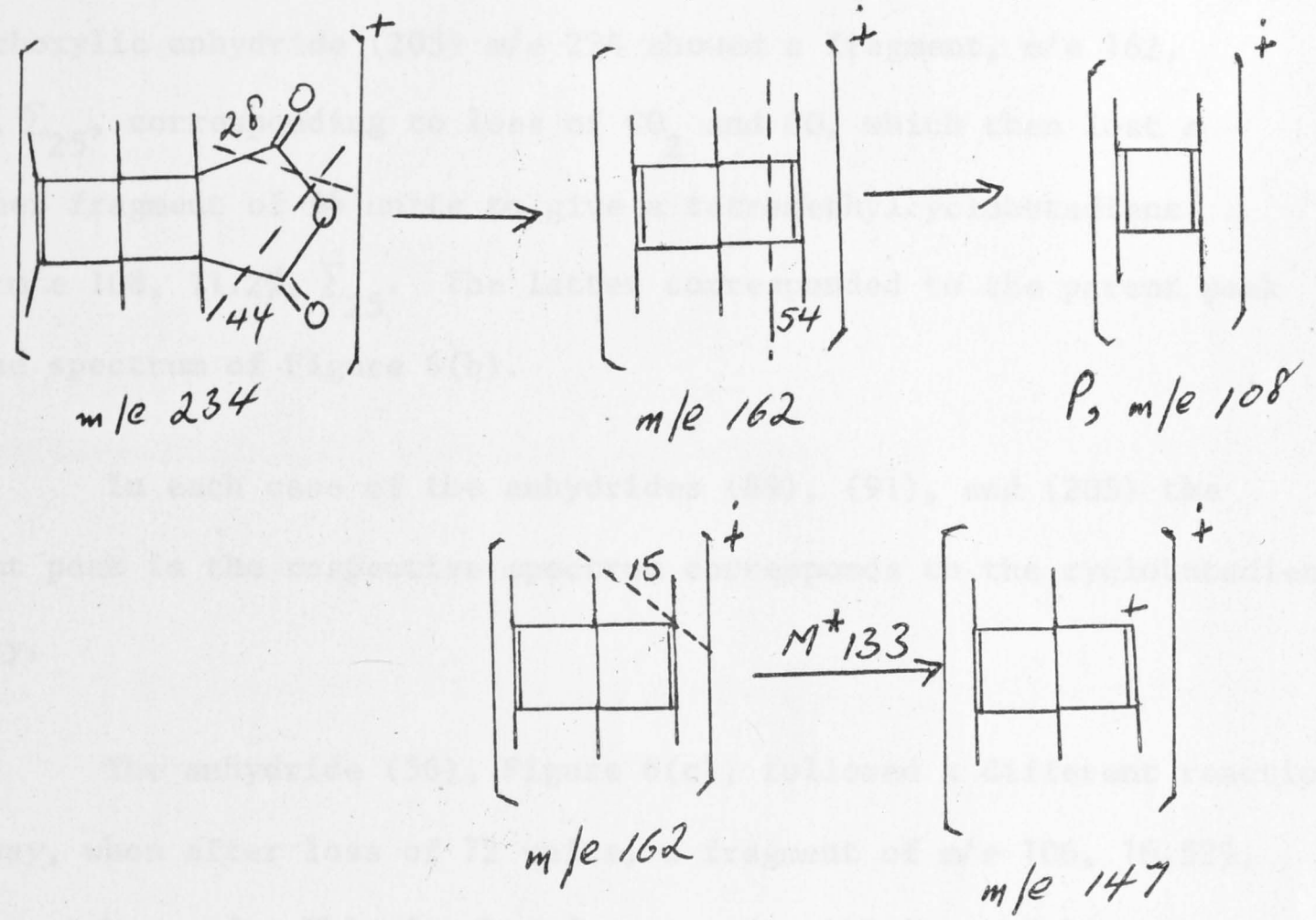
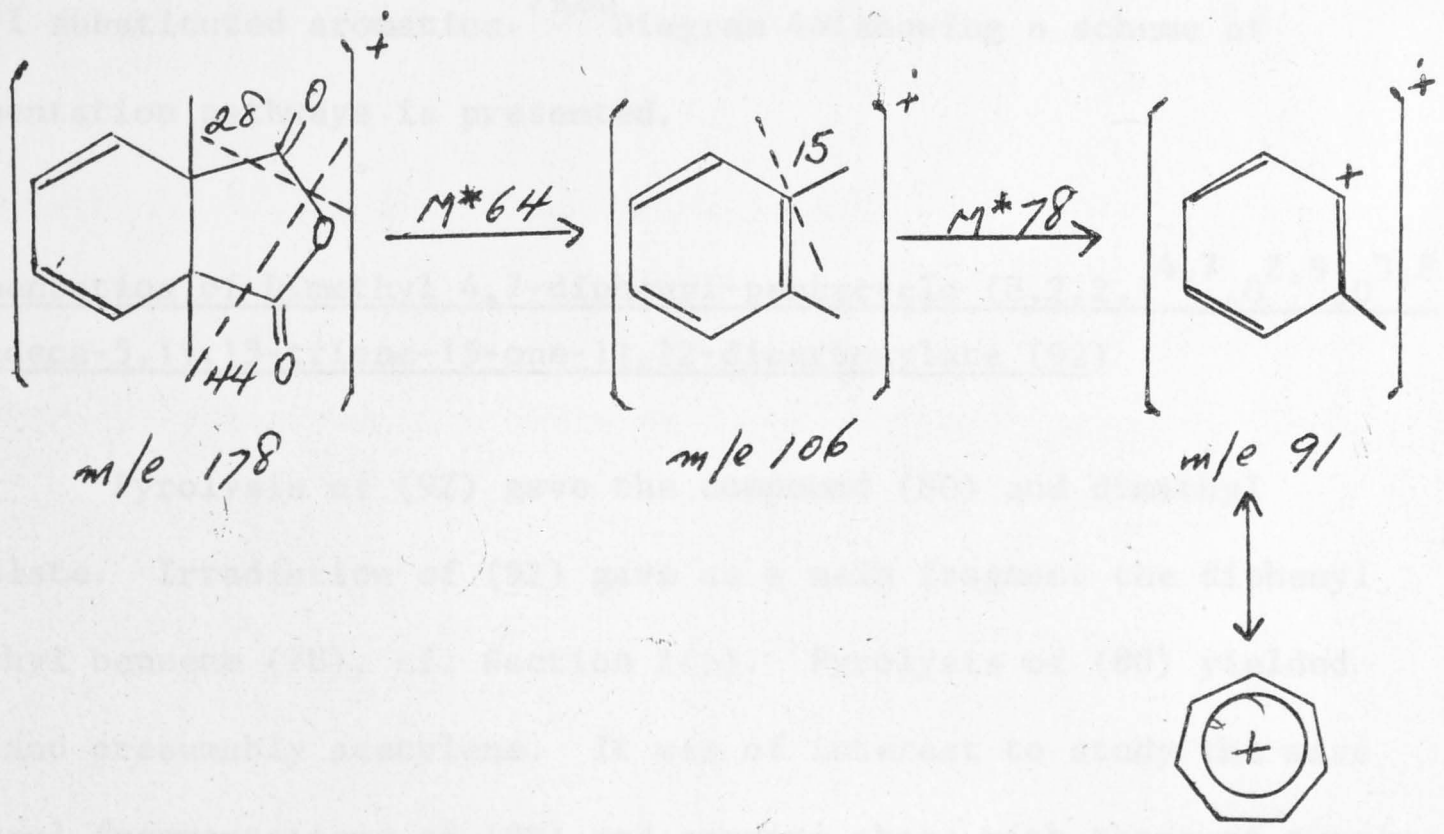


DIAGRAM 44

(c) 1,2,3,4,5,6-hexamethyl-bicyclo (2,2,1)hex-2-ene-5,6 dicarboxylic anhydride (205)



(d) 5,6-dimethyl-cyclohexa-1,3-diene-5,6-dicarboxylic anhydride (56)



1,2,3,4,5,6-hexamethyl-bicyclo (2,2,1) hex-2-ene-5,6-dicarboxylic anhydride (205) m/e 234 showed a fragment, m/e 162, 8.3%, Σ_{25}, corresponding to loss of CO_2 and CO, which then lost a further fragment of 54 units to give a tetramethylcyclobutadiene ion, m/e 108, 11.2%, Σ_{25}. The latter corresponded to the parent peak in the spectrum of Figure 6(b).

In each case of the anhydrides (89), (91), and (205) the parent peak in the respective spectrum corresponds to the cyclobutadiene moiety.

The anhydride (56), Figure 6(c), followed a different reaction pathway, when after loss of 72 units, a fragment of m/e 106, 16.52%, Σ_{25}, was observed. This further fragmented, with loss of 15 units to a parent peak a fragment of m/e 91, 23.55%, Σ_{25}, corresponding to the tropylium ion. This is commonly observed in the fragmentation of methyl substituted aromatics.[79,80] Diagram 44d showing a scheme of fragmentation pathways is presented.

Fragmentation of Dimethyl 4,7-diphenyl-pentacyclo ($8,2,2,1^{4,7},0^{2,9},0^{3,8}$) pentadeca-5,11,13-triene-15-one-11,12-dicarboxylate (92)

Pyrolysis of (92) gave the compound (80) and dimethyl phthalate. Irradiation of (92) gave as a main fragment the diphenyl dimethyl benzene (78), cf. Section 2(b). Pyrolysis of (80) yielded (78) and presumably acetylene. It was of interest to study the mass spectral fragmentations of (92) and compare these with those of pyrolysis

and of photolysis. A simplified mass spectrum of (92) is to be found in Figure 6(a). A scheme is presented in Diagram 45 of what appeared to be the main fragmentation pathway of (92). It follows the pyrolytic reaction sequence of rupture of the cyclobutane ring in (92).

Fragmentation of cis-3,4-dichloro-cyclobutene (50)

A simplified mass spectrum of (50) is shown in Figure 4(a).

The compound (50) m/e 122 fragmented with loss of 35 units to give a parent peak fragment m/e 87, 26.6%, Σ_{25}. There was a further loss of 36 units to give a fragment m/e 51, 18%, Σ_{25}. This corresponded to a two-step loss of chlorine atoms. The last step apparently removed the chlorine as hydrogen chloride. There was a further fragment m/e 26, 5.5%, Σ_{25}, corresponding to an acetylene ion. A scheme is presented in Diagram 46 for the fragmentation of (50).

Fragmentation of cis-trans-muconic acid (208)

A simplified mass spectrum of (208) is shown in Figure 5(a). A scheme is presented in Diagram 47 for the fragmentation of (208).

DIAGRAM 45

4,7-diphenyl-pentacyclo (8,2,2,$1^{4,7}$,$0^{2,9}$,$0^{3,8}$) pentadeca-5,11,13-triene-15-one-11,12-dicarboxylate (92)

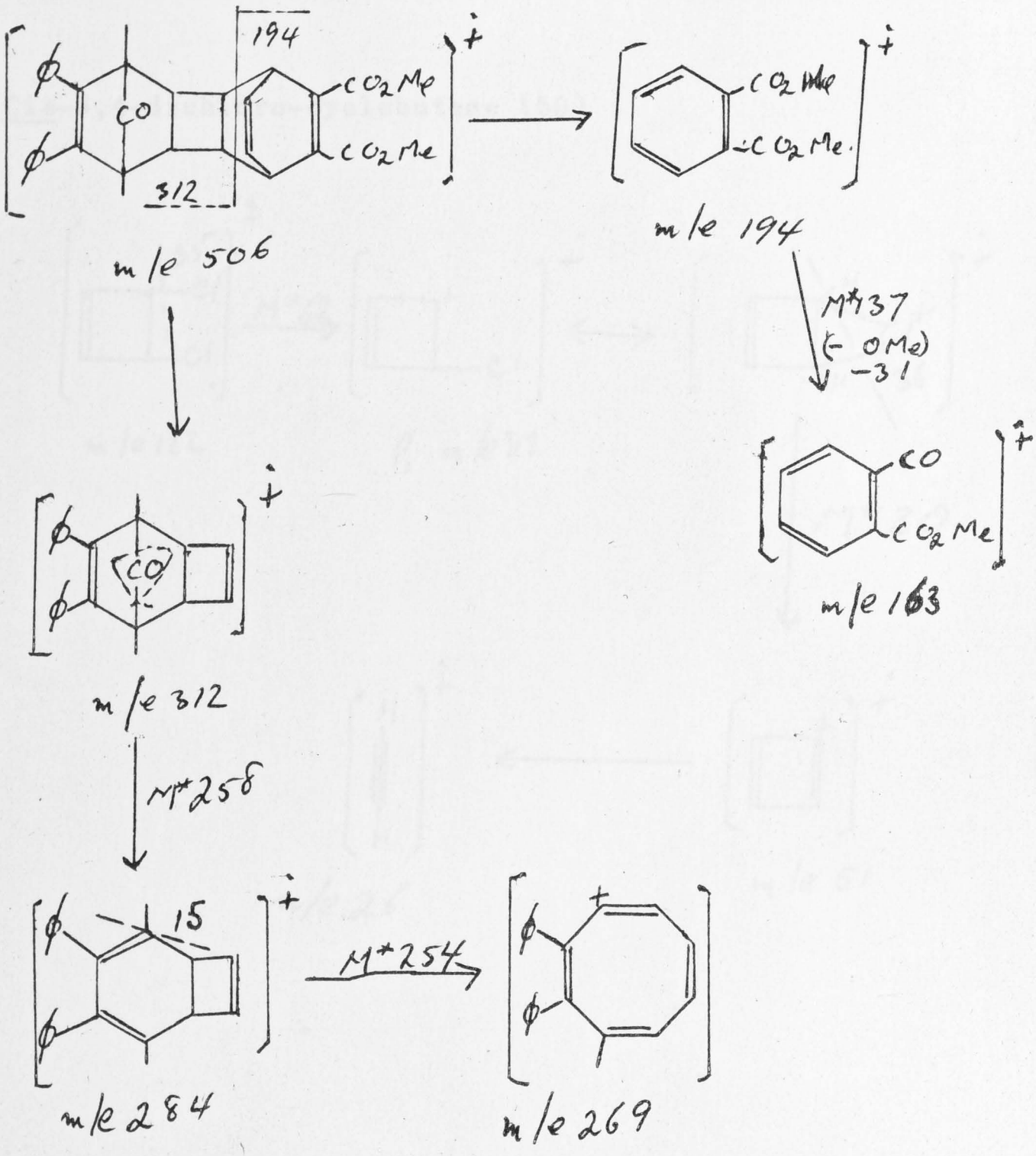


DIAGRAM 46

Cis-3,4-dichloro-cyclobutene (50)

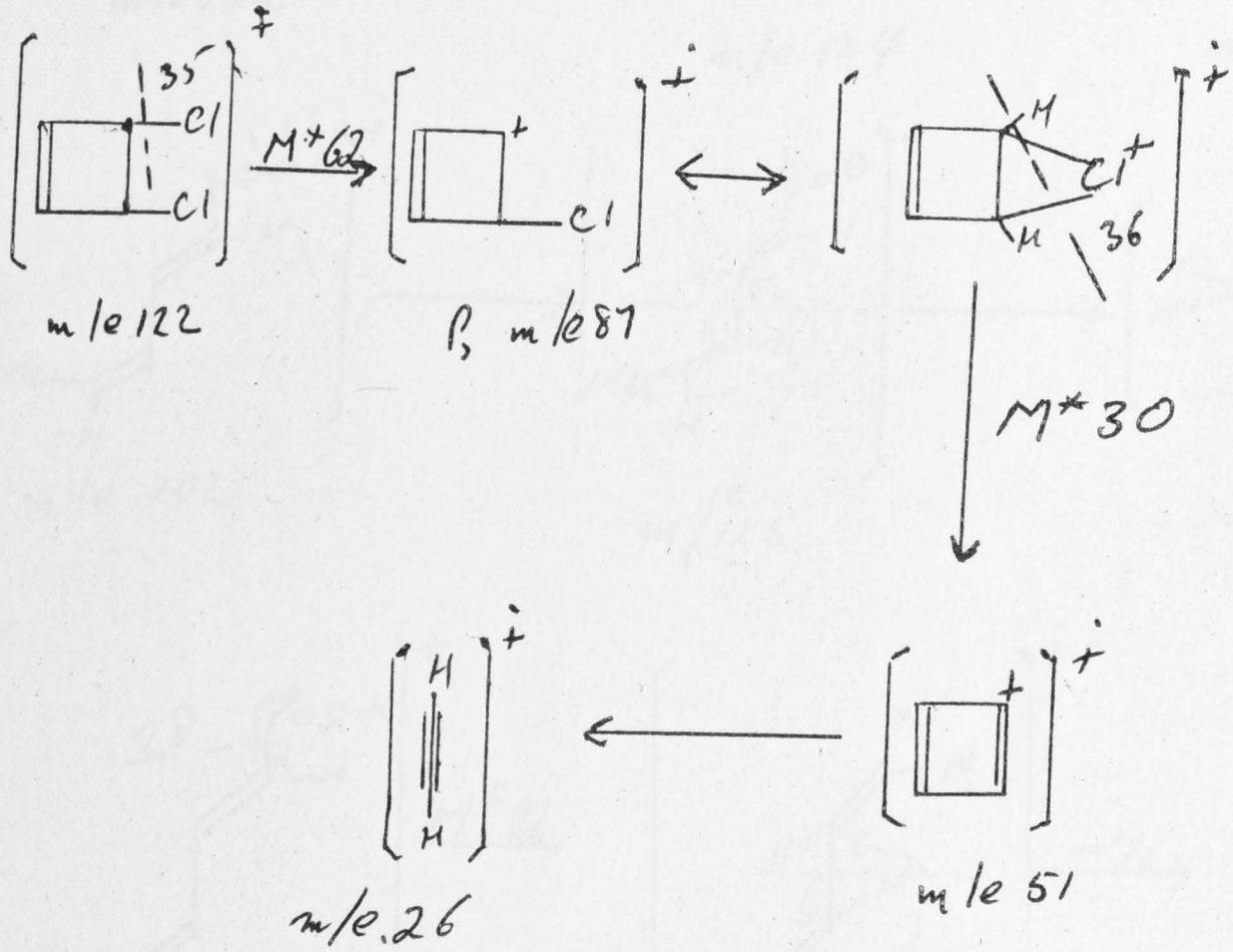


DIAGRAM 47

Cis-trans-muconic acid (208)

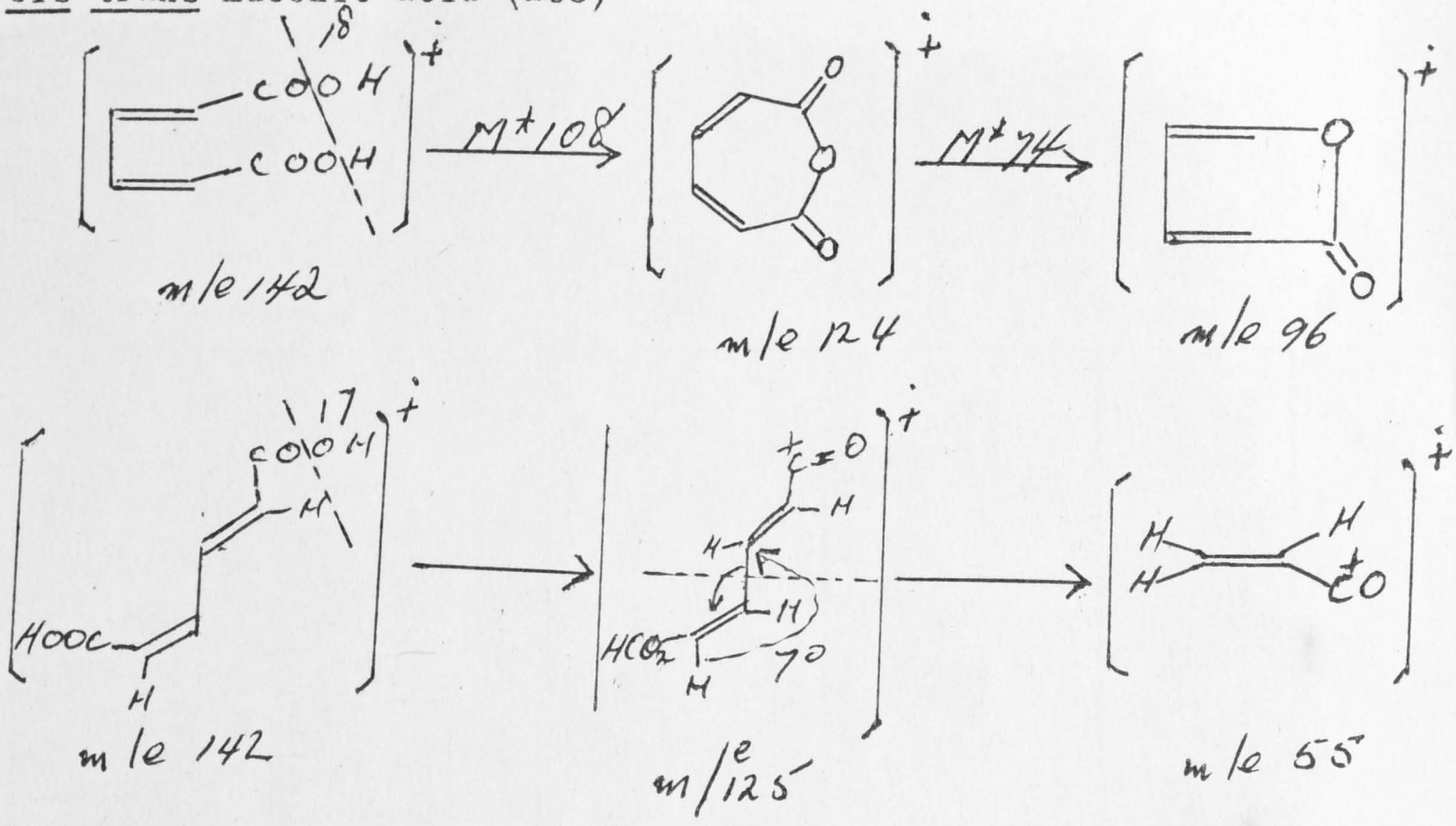


FIGURE 1.

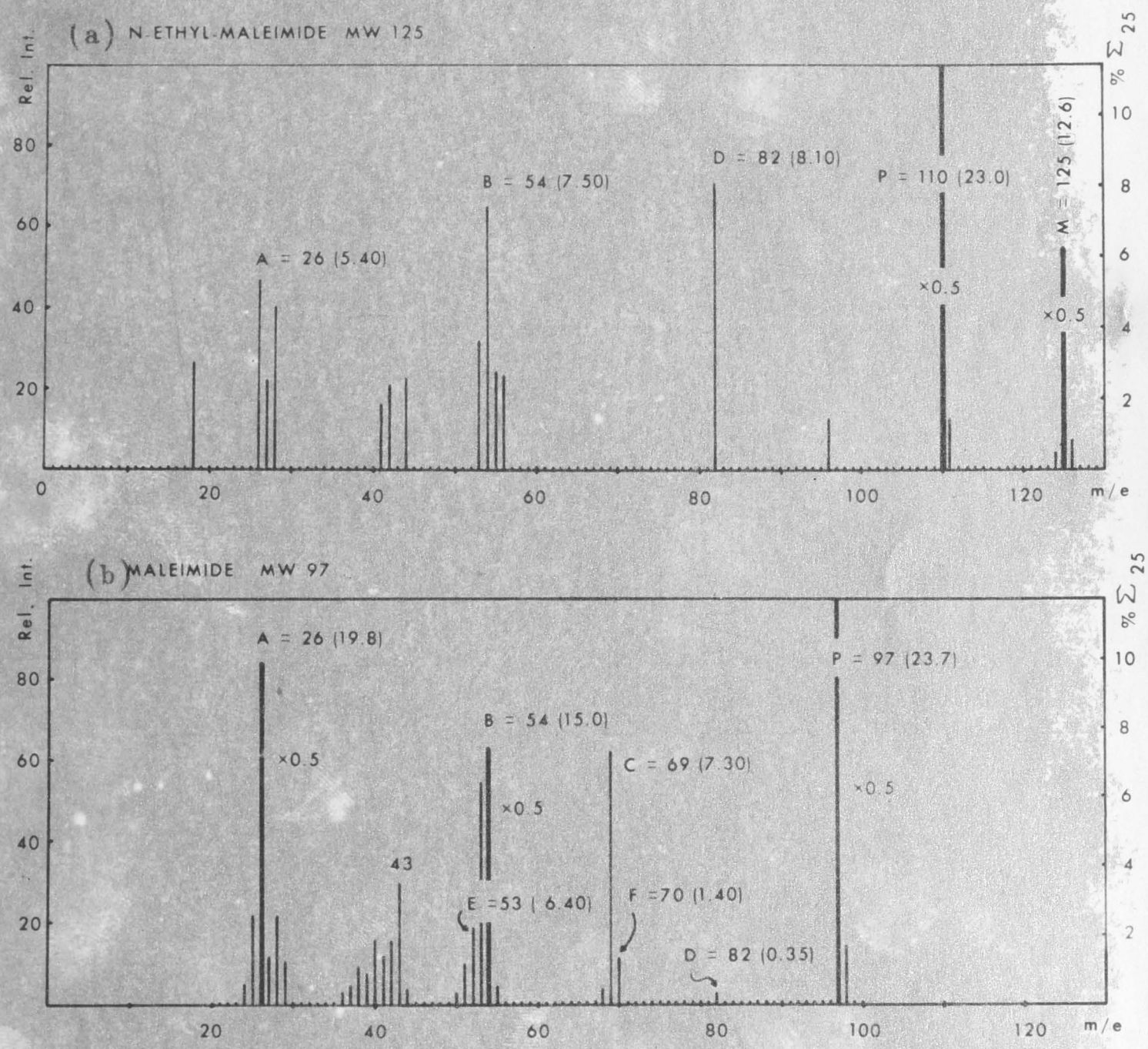
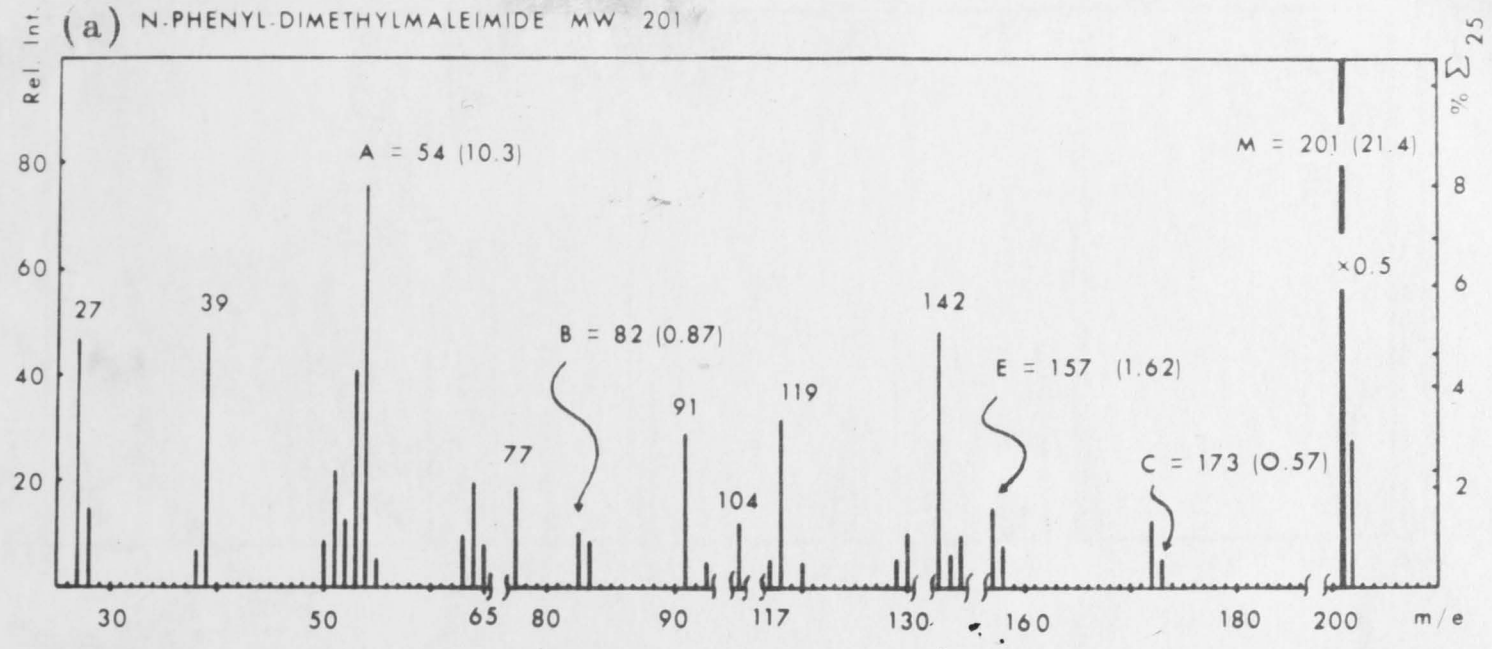
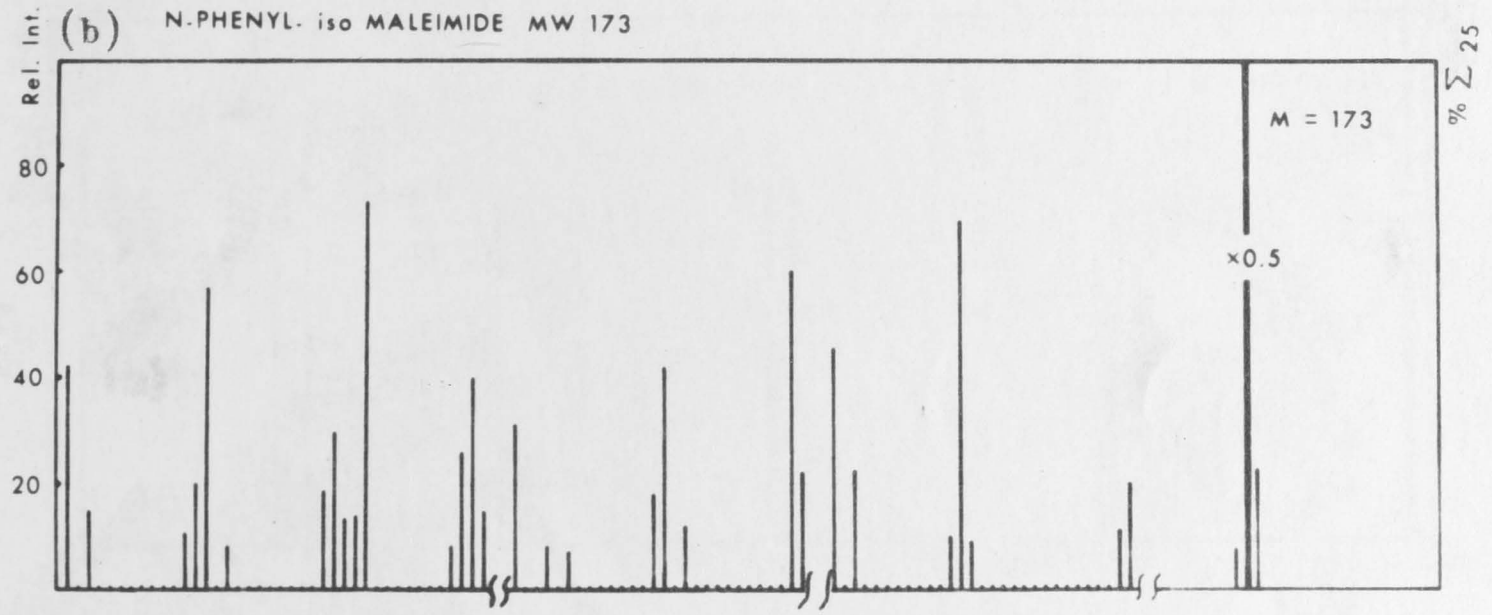

(a) N-ETHYL-MALEIMIDE MW 125
Rel. Int.
80
60
40
20
0
20
40
60
80
100
120
m/e
A = 26 (5.40)
B = 54 (7.50)
D = 82 (8.10)
P = 110 (23.0)
M = 125 (12.6)
×0.5
×0.5
Σ 25
%
10
8
6
4
2
(b) MALEIMIDE MW 97
Rel. Int.
80
60
40
20
20
40
60
80
100
120
m/e
A = 26 (19.8)
×0.5
B = 54 (15.0)
×0.5
43
E = 53 (6.40)
C = 69 (7.30)
F = 70 (1.40)
D = 82 (0.35)
P = 97 (23.7)
×0.5
Σ 25
%
10
8
6
4
2

FIGURE 2.


(a) N-PHENYL-DIMETHYLMALEIMIDE MW 201
Rel. Int.
% Σ 25
A = 54 (10.3)
M = 201 (21.4)
×0.5
27
39
B = 82 (0.87)
142
E = 157 (1.62)
91
119
77
104
C = 173 (0.57)
80
60
40
20
8
6
4
2
30
50
65
80
90
117
130
160
180
200
m/e


(b) N-PHENYL- iso MALEIMIDE MW 173
Rel. Int.
% Σ 25
M = 173
×0.5
80
60
40
20

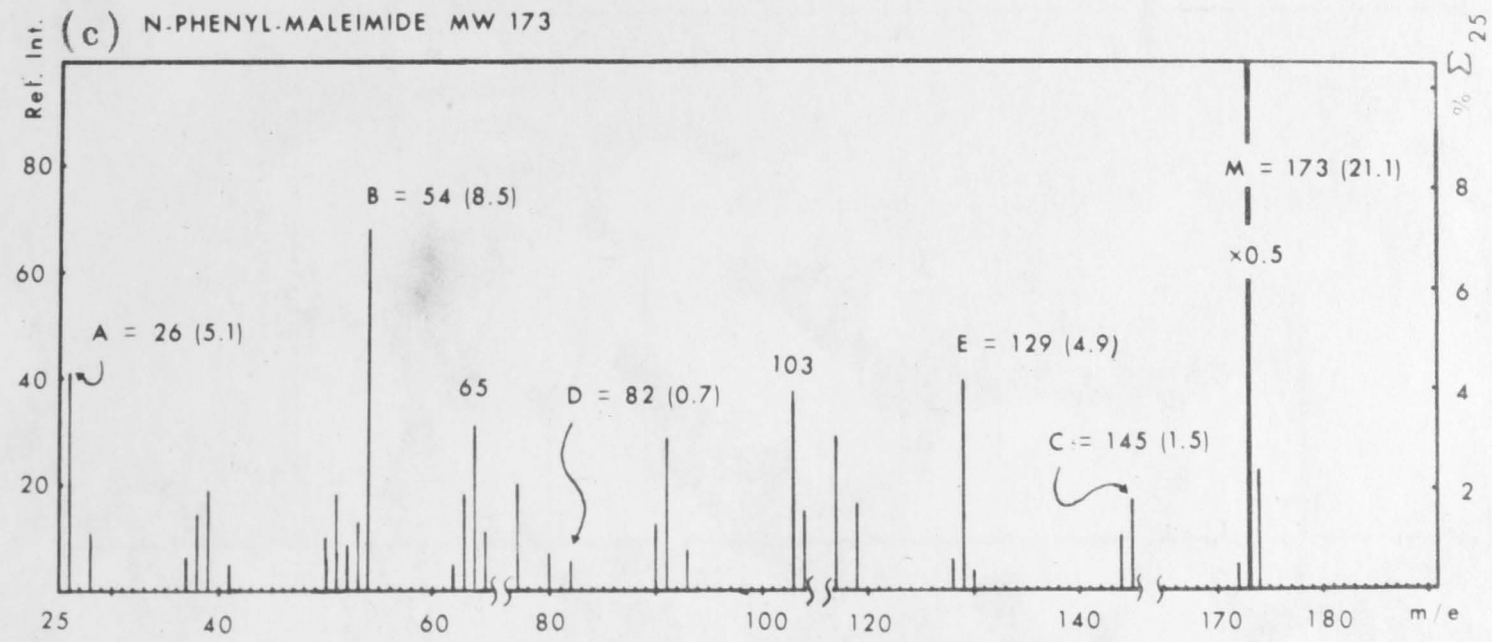
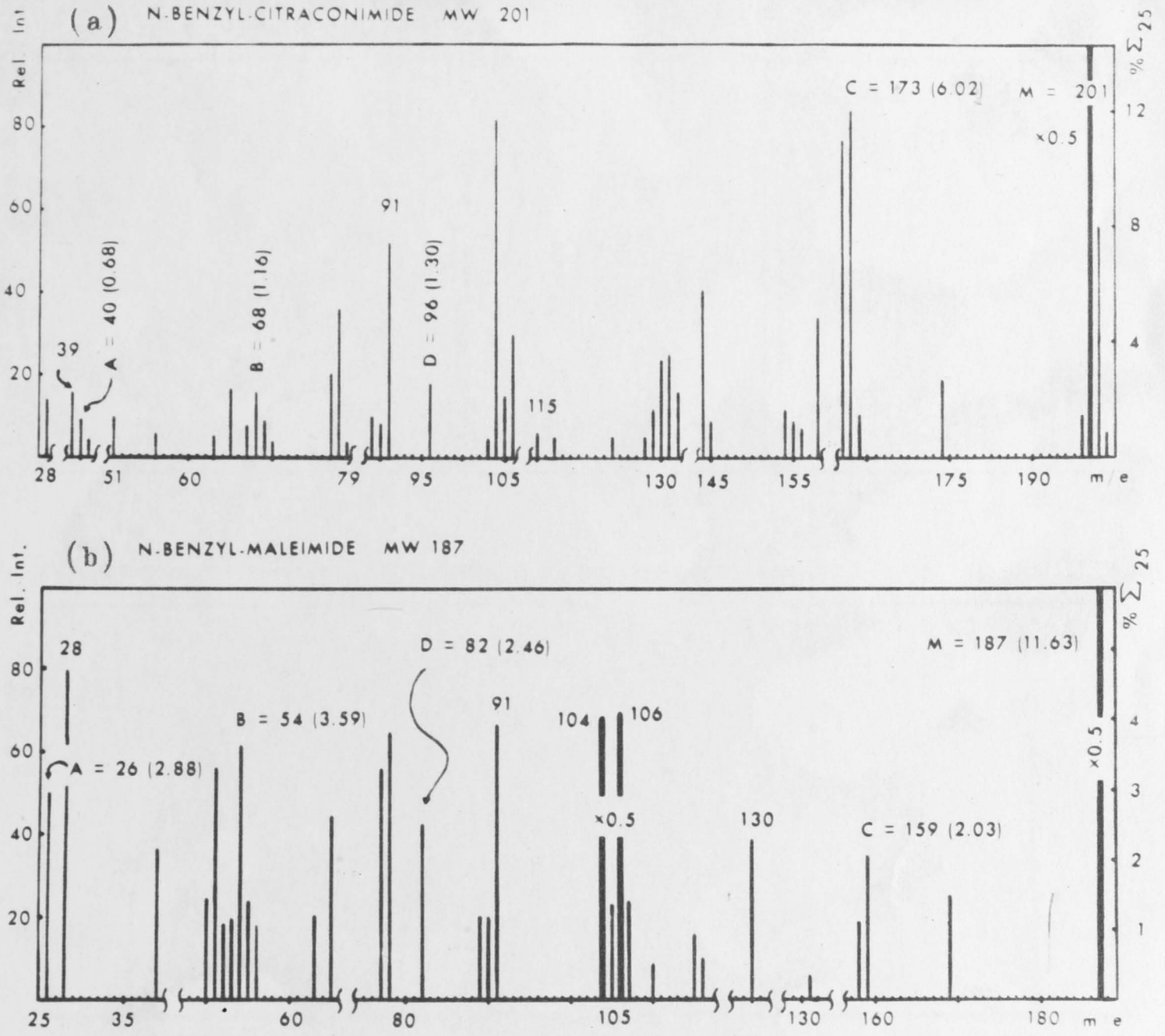

(c) N-PHENYL-MALEIMIDE MW 173
Ref. Int.
% Σ 25
M = 173 (21.1)
×0.5
B = 54 (8.5)
A = 26 (5.1)
65
D = 82 (0.7)
103
E = 129 (4.9)
C = 145 (1.5)
80
60
40
20
8
6
4
2
25
40
60
80
100
120
140
170
180
m/e

FIGURE 3.


(a) N-BENZYL-CITRACONIMIDE MW 201
Rel Int
% Σ 25
C = 173 (6.02)
M = 201
×0.5
A = 40 (0.68)
B = 68 (1.16)
D = 96 (1.30)
91
39
115
28 51 60 79 95 105 130 145 155 175 190 m/e

(b) N-BENZYL-MALEIMIDE MW 187
Rel. Int.
% Σ 25
28
D = 82 (2.46)
M = 187 (11.63)
B = 54 (3.59)
91
104
106
A = 26 (2.88)
×0.5
130
C = 159 (2.03)
25 35 60 80 105 130 160 180 m/e

(c) N-BENZYL-CYCLOBUTENE-cis-3, 4-DICARBOXIMIDE MW 213
Rel. Int.
% Σ 25
A = 52 (18.5)
B = 80 (3.78)
D = 108 (4.92)
M = 213 (10.4)
91
132
65
25 40 60 80 105 130 150 175 210 m/e

FIGURE 4.

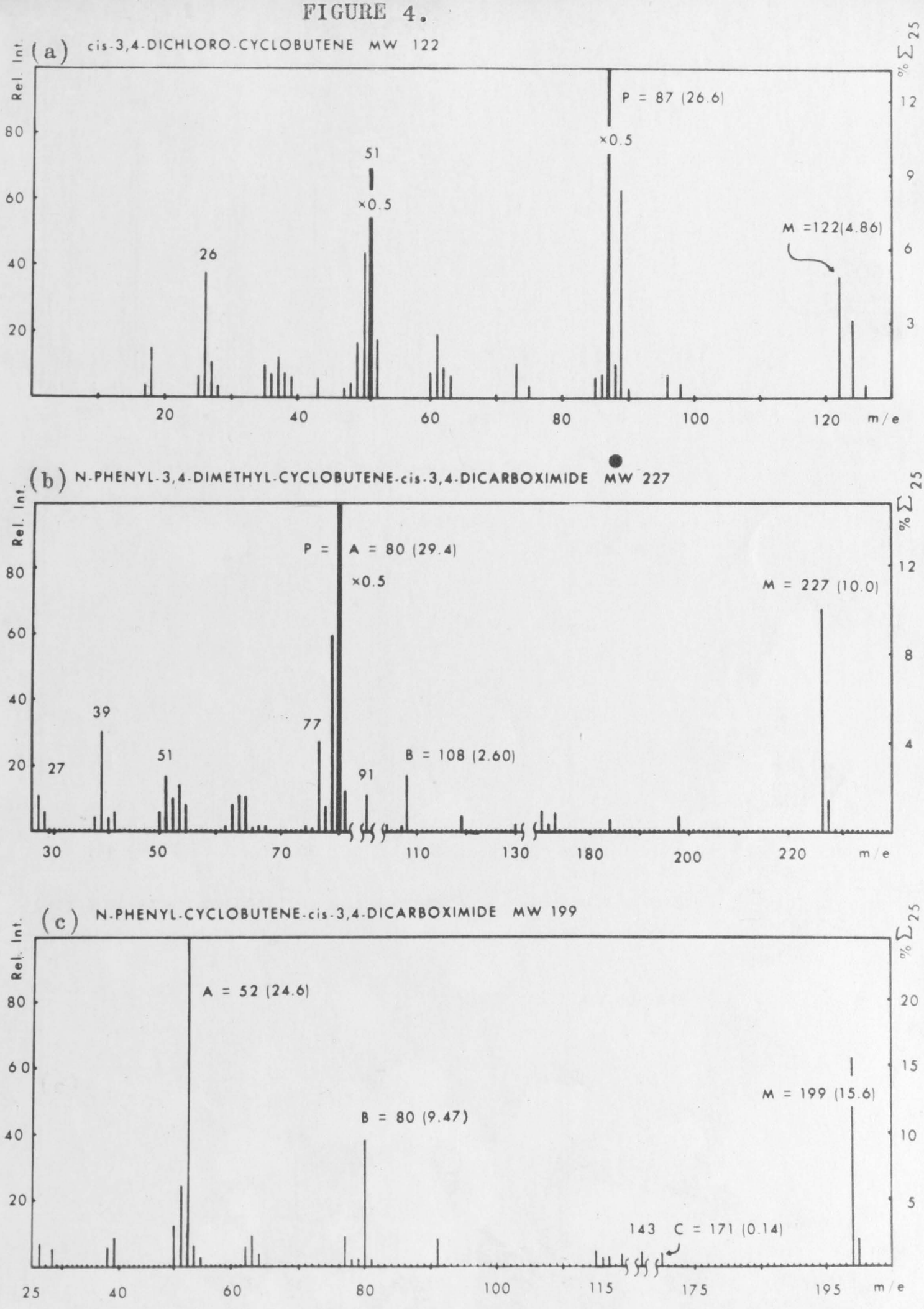

(a) cis-3,4-DICHLORO-CYCLOBUTENE MW 122
Rel. Int.
% Σ 25
P = 87 (26.6)
×0.5
51
×0.5
M =122(4.86)
26
80
60
40
20
12
9
6
3
20
40
60
80
100
120
m/e
(b) N-PHENYL-3,4-DIMETHYL-CYCLOBUTENE-cis-3,4-DICARBOXIMIDE MW 227
P =
A = 80 (29.4)
×0.5
M = 227 (10.0)
39
77
51
27
91
B = 108 (2.60)
8
4
30
50
70
110
130
180
200
220
(c) N-PHENYL-CYCLOBUTENE-cis-3,4-DICARBOXIMIDE MW 199
A = 52 (24.6)
M = 199 (15.6)
B = 80 (9.47)
143 C = 171 (0.14)
60
15
10
5
25
40
60
80
100
115
175
195

FIGURE 5.

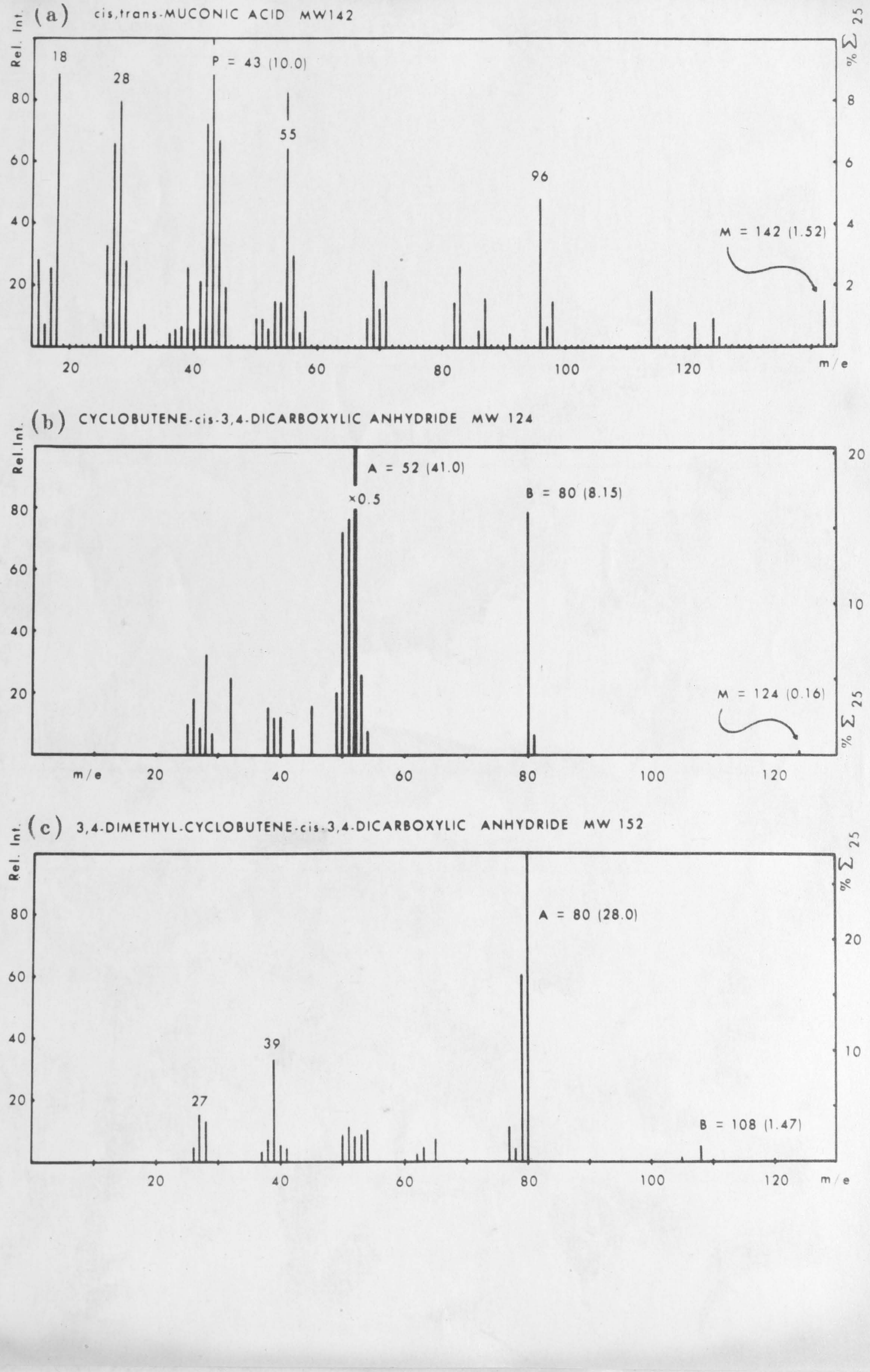
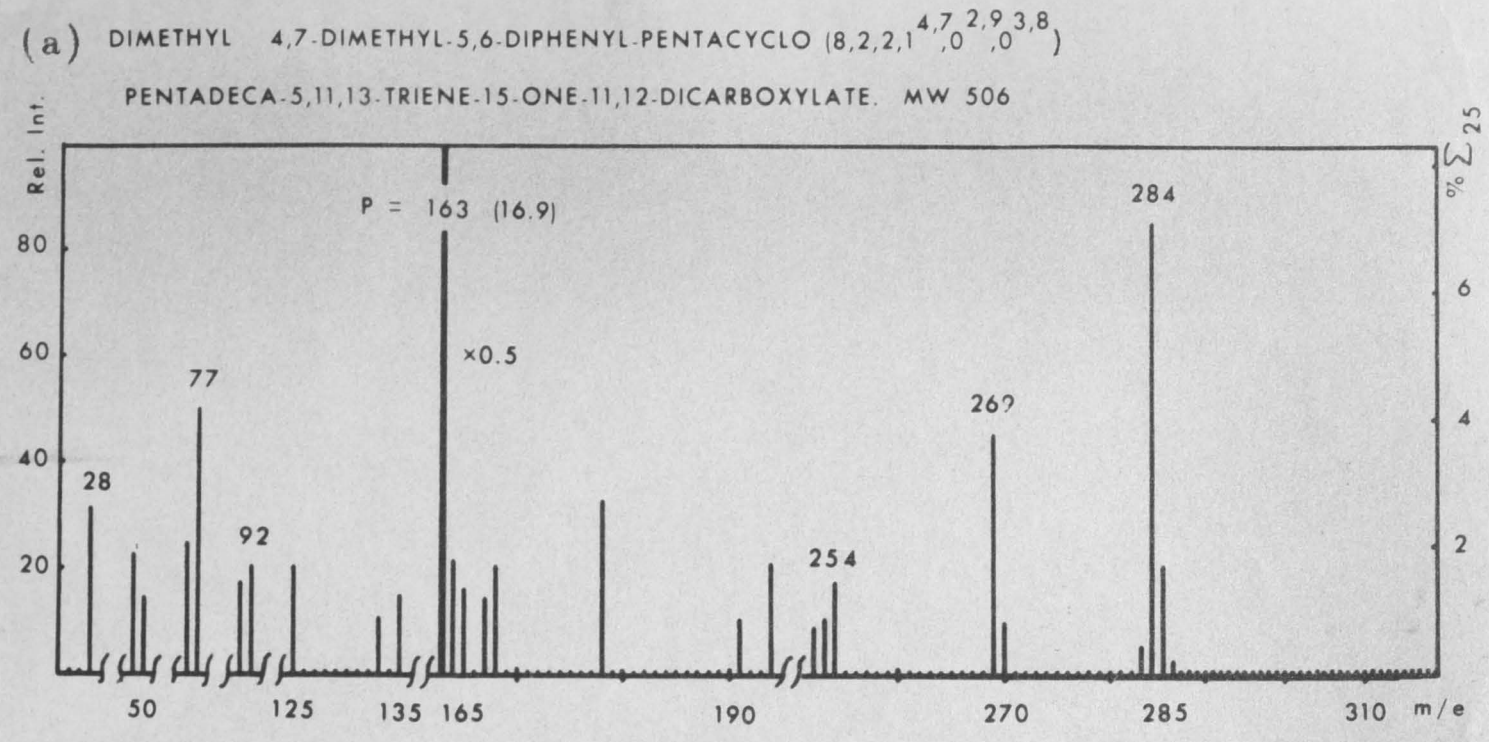
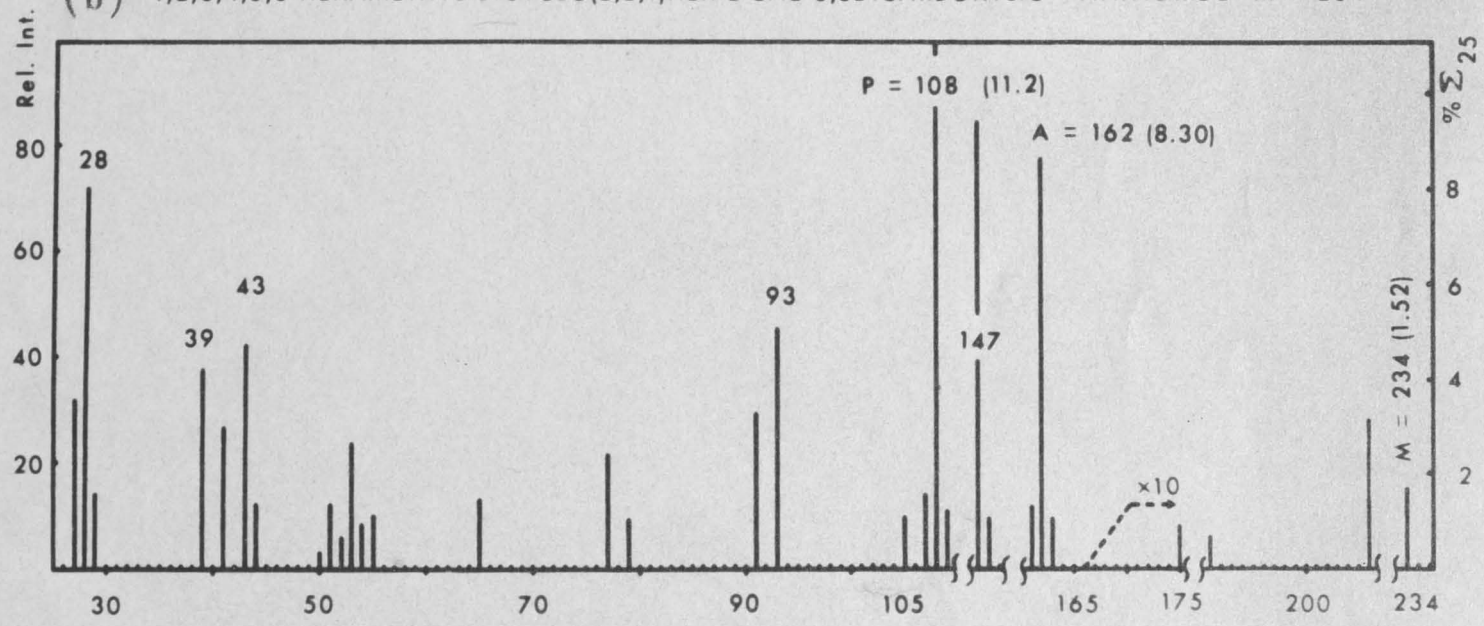
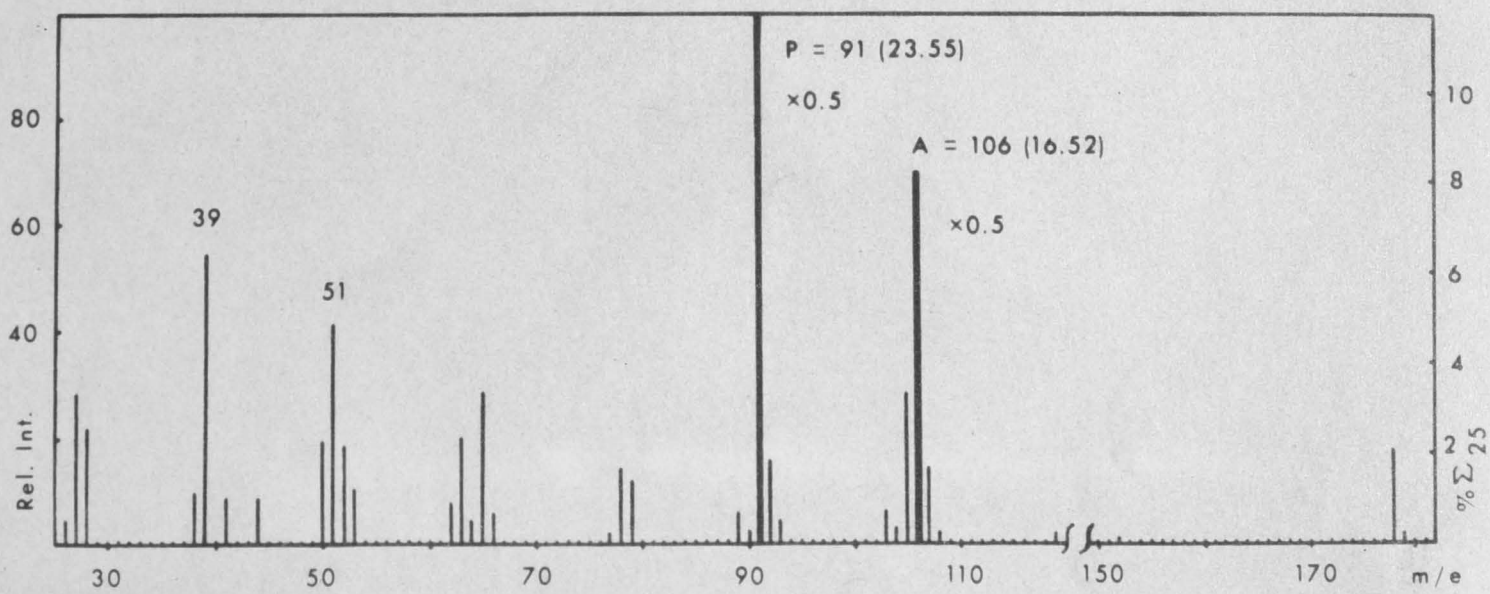

(a) cis,trans-MUCONIC ACID MW142
Rel. Int.
% Σ 25
18
28
P = 43 (10.0)
55
96
M = 142 (1.52)
m/e
(b) CYCLOBUTENE-cis-3,4-DICARBOXYLIC ANHYDRIDE MW 124
Rel.Int.
A = 52 (41.0)
×0.5
B = 80 (8.15)
M = 124 (0.16)
m/e
(c) 3,4-DIMETHYL-CYCLOBUTENE-cis-3,4-DICARBOXYLIC ANHYDRIDE MW 152
Rel. Int.
A = 80 (28.0)
39
27
B = 108 (1.47)
m/e

FIGURE 6.


(a) DIMETHYL 4,7-DIMETHYL-5,6-DIPHENYL-PENTACYCLO (8,2,2,1^{4,7},0^{2,9},0^{3,8})
PENTADECA-5,11,13-TRIENE-15-ONE-11,12-DICARBOXYLATE. MW 506
Rel. Int.
% Σ 25
P = 163 (16.9)
×0.5
284
269
254
77
28
92
80
60
40
20
6
4
2
50
125
135 165
190
270
285
310 m/e


(b) 1,2,3,4,5,6-HEXAMETHYL-BICYCLO(2,2,1)HEX-2-ENE-5,6DICARBOXYLIC ANHYDRIDE MW 234
Rel. Int.
% Σ 25
P = 108 (11.2)
A = 162 (8.30)
M = 234 (1.52)
28
43
39
93
147
×10
80
60
40
20
8
6
4
2
30
50
70
90
105
165
175
200
234


(c) 5,6-DIMETHYL-CYCLOHEXA-1,3-DIENE-5,6-DICARBOXYLIC ANHYDRIDE MW 178
P = 91 (23.55)
×0.5
A = 106 (16.52)
×0.5
39
51
Rel. Int.
% Σ 25
80
60
40
10
8
6
4
2
30
50
70
90
110
150
170
m/e

SECTION 5

EXPERIMENTAL

Experimental (General)

All new compounds have been underlined at their first mention in the text in the following Experimental Section. Analyses were made by the Commonwealth Scientific Industrial Research Organisation Microanalytical Laboratories, Melbourne, under the direction, formerly of Dr. K.W. Zimmermann; and now of Dr. L.W. McDonald.

Nuclear magnetic resonance (n.m.r.) spectra (H^1) were determined using a Perkin-Elmer R 10 Spectrometer operating at 60 megacycles/second. Deuterated chloroform was used as the solvent unless otherwise stated, and values are quoted with reference to tetramethylsilane as an internal standard.

Infra-red absorption spectra were obtained using a Unicam S.P. 200 Spectrophotometer. The compounds were suspended in nujol mulls unless stated otherwise.

Qualitative ultraviolet absorption spectra were obtained, using A Unicam S.P. 800 Spectrophotometer, with the compounds dissolved in ethanol (90%), in 1 cm quartz cells.

ϵ values were obtained in ethanol (96%) using an Hitachi model EPS-3T Recording Spectrophotometer.

Melting points (uncorrected) were determined by a Gallenkamp Melting Point Apparatus with the compounds placed in open capilliary tubes.

The silica gel (100/200 mesh) used for column chromatography was obtained from Koch-Light Laboratories Ltd., England.

All solvents used in chromatography, and as media for the reactions, were purified before use.

1. Preparation of Cis-1,2-Dimethyl-Cyclohex-4-Ene 1,2 Dicarboxylic Anhydride (57)

The compound (57) was prepared by heating buta-1,3-diene, and dimethylmaleic anhydride (44) together in a sealed vessel after Ziegler's method.[23] The working up and isolation however, was carried out after Woodward's procedure.[22]

Dimethylmaleic anhydride (20g) and buta-1,3-diene (9.1g) were placed in the Aminco High-Pressure Assembly, together with a quantity of clean copper turnings, and heated at 160^{o} for about 37 hours.

After cooling, and release of slight pressure, the material in the bomb was extracted and worked up according to Woodward's procedure.

The compound, cis-1,2-dimethyl-cyclohex-4-ene 1,2 dicarboxylic anhydride (57) was obtained, after repeated recrystallisations from n-hexane, as small, colourless crystals. Yield, 12g (41%); melting point 99° (literature 100°). (Found: C, 67.8; H, 5.9; O, 26.1%. Calculated for $C_{10}H_{12}O_3$, C, 67.4; H, 5.7; O, 26.1%.)

The n.m.r. spectrum had τ = 4.08 (2H, multiplet, base = 10 cps, vinyl H); τ = 7.32 (2H, doublet, J = 12 cps, each doublet peak a multiplet, ring methylene H), τ = 8.01 (2H, doublet, J = 12 cps, each doublet peak a multiplet), and τ = 8.64 (6H, singlet, methyl H).

The infra-red spectrum had main bands at ν_{max}: 1830w, 1770s, 1285m, 1260m, 1220m, 1000s, 980s, 910m, 750m, and at 690s cm^{-1}.

2. Preparation of Cis-1,2-Dimethyl-4,5-Dibromo-Cyclo Hexane Dicarboxylic Anhydride (58)

Cis-1,2-dimethyl-cyclohex-4-ene 1,2-dicarboxylic anhydride (57) (1g) was dissolved in the minimum quantity of acetic acid, and bromine (1g) was added dropwise to the solution, with constant stirring and cooling (10°).

After a few minutes the compound cis-1,2-dimethyl-4,5-dibromo-cyclohexane-1,2-dicarboxylic anhydride (58) began to crystallise out. On the completion of bromine addition the mixture was set aside overnight.

The precipitate was filtered off at the water pump and sucked free of bromine and acetic acid.

Several recrystallisations from ether/chloroform gave the compound (58) in 95% yield, melting point, 180° (literature 179-180°).[22]

The infra-red spectrum had main bands at ν_{max}: 1835w, 1780s (anhydride), 1245s, 1195s, 1170m, 1080m, 965s, 935s, and at 730m cm^{-1}.

The n.m.r. spectrum had τ = 5.86 (1H, multiplet, base = 8 cps, tertiary H), τ = 6.03 (1H, multiplet, base = 8 cps, tertiary H), τ = 6.99 (2H, doublet, J = 14 cps, each doublet peak a multiplet, ring methylene H), τ = 7.62 (2H, doublet, J = 14 cps, each doublet peak a multiplet, ring methylene H), τ = 8.63 (3H, singlet, methyl H), and τ = 8.70 (3H, singlet, methyl H).

3. Attempted Preparation of Cis-1,2-Dimethyl-3,5-Cyclohexadiene 1,2-Dicarboxylic Anhydride (56), According to the Procedure of Ziegler and Co-Workers[23]

First Attempt

Cis-1,2-dimethyl,4,5 dibromo-cyclohexane 1,2 dicarboxylic anhydride (58) (2g) was heated in s-collidine (200 ml) to 155°, and the compound, 1,2-dimethyl-cyclohexa-3,5-diene 1,2 dicarboxylic anhydride (56) isolated according to the procedure described by Ziegler to give a yield of 18% (160mg).

Second Attempt

The compound (58) (1g) was added slowly, in small increments, to s-collidine (200 ml) kept at 155° and the compound (56) was isolated according to the procedure mentioned to give a 20% (100mg) yield.

Other Attempts

Five more reactions of 1,2-dimethyl-4,5-dibromo-cyclohexane-1,2-dicarboxylic anhydride (58) were carried out, according to the described procedure. The yields of cis-1,2-dimethyl-cyclohexa-3,5-diene-1,2-dicarboxylic anhydride (56) varied from 10% to 20%.

4. Preparation of Cis-1,2-Dimethyl-3-Bromo-Cyclohex-4-Ene Dicarboxylic Anhydride (59)

Cis-1,2-dimethyl-cyclohex-4-ene dicarboxylic anhydride (57) (1g), and N-bromo-succinimide (1g) were dissolved in dry carbon tetrachloride (15 ml) and gently refluxed for about 6 hours.

The solution was cooled, filtered, and the carbon tetrachloride evaporated off carefully under reduced pressure at room temperature. The viscous residue crystallised with chilling. Sublimation at room temperature/1mm gave the compound cis-1,2-dimethyl-3-bromo-cyclohex-4-ene-1,2-dicarboxylic anhydride (59) in 90% yield; melting point 50° (literature 50-53°).[23]

The infra-red spectrum had main bands at ν_{max}: 1850w, 1790s (anhydride), 1220s, 975s, 950s, 775s, 735m, and at 710w cm^{-1}.

5. Attempted Preparation of Cis-1,2-Dimethyl-Cyclohexa-3,5-Diene 1,2-Dicarboxylic Anhydride (56) By Dehydrobromination of Cis-1,2-Dimethyl-3-Bromo-Cyclohexa-3,5-Diene-1,2-Dicarboxylate Anhydride (59)

First Attempt

Cis-1,2-dimethyl-3-bromo-cyclohexa-3,5-diene-1,2-dicarboxylic anhydride (59) (300 mg) in solution in s-collidene (100 ml), was set aside for 3 days, under an atmosphere of nitrogen. The solution became dark-brown and slightly turbid. The extraction procedure was according to ethereal hydrogen chloride solution procedure described in Section 5 (6). After removal of the ether and residual hydrogen chloride, examination by infra-red spectroscopy of the residue obtained, indicated that there was none of the compound (56) present.

Second Attempt

The above mentioned compound (59) (1g) was added in small increments to s-collidine (100 ml) at a temperature 155^{o} over 30 minutes. The solution became dark brown. The extraction procedure was according to the ethereal hydrogen chloride solution procedure described in Section 5 (6). After removal of the ether and residual

hydrogen chloride, examination by infra-red spectroscopy of the residue obtained, indicated that there was none of the compound (56) present.

6. Preparation of Cis-1,2-Dimethyl-Cyclohexa-3,5-Diene-1,2-Dicarboxylic Anhydride (56) by Dehydrobromination with 1,5-Diaza-Bicyclo (4,3,0) Nona-5-One (60)

First Procedure

Cis-1,2-dimethyl-3-bromo-cyclohex-4-ene dicarboxylic anhydride (59) (1g) was dissolved in dry acetone (3 ml), and 1,5-diaza-bicyclo (4,3,0) nona-5-ene (60) (2g) was added in dropwise fashion, under an atmosphere of nitrogen, to the solution with stirring, and cooling (0^{o}). On the completion of the addition of the compound (60) the solution was set aside under an atmosphere of nitrogen at room temperature overnight.

A saturated solution of hydrogen chloride in anhydrous ether was added slowly to the reaction mixture, with cooling (0^{o}). The hydrochloride of the compound (56) separated out. When there was no further separation the ethereal solution was filtered off, and the ether carefully evaporated from the filtrate, under reduced pressure at room temperature.

Thin layer chromatography of the residue on silica gel with benzene as solvent showed a single mobile spot R_f 0.65 with material left at the origin.

The fractions were collected, and the solvent evaporated off, at room temperature under reduced pressure (20mm), to a small volume when cis-1,2-dimethyl-cyclohexa-3,5-diene-1,2-dicarboxylic anhydride crystallised out.

Sublimation of the compound (56) gave a yield 0.45g (45%). Melting point, 71° (literature 70°).[23] (Found: C, 67.8; H, 6.0; O, 26.1%. Calculated for $C_{10}H_{10}O_3$: C, 67.4; H, 5.7; O, 26.9%.) The infra-red spectrum had main bands at ν_{max}: 1855w, 1785s (anhydride), 1225m, 1190m, 965s, 910s, 710m, and at 670m cm^{-1}. The n.m.r. spectrum had τ = 3.9 (2H, multiplet, vinyl H), τ = 4.26 (2H, multiplet, vinyl H), and τ = 8.62 (6H, singlet, methyl H). The ultraviolet spectrum had a λ_{max}: = 260 mμ .

Second Procedure

Cis-1,2-dimethyl-3-bromo-cyclohex-4-ene-1,2-dicarboxylic anhydride (59) (1g), and 1,5-diazo-bicyclo (4,3,0) nona-5-ene (60) (2g) were reacted together as described in the first procedure.

The reaction mixture was dissolved in 150 ml sulphuric acid, and extracted with ether. The ether was dried over magnesium sulphate overnight, and then filtered. The filtrate was evaporated

at room temperature under reduced pressure. The compound, cis-1,2-dimethyl-cyclohexa-3,5-diene-1,2-dicarboxylic acid crystallised out. Yield: 1.03g (100%).

The free acid of (56) was gently refluxed with benzene with toluene-sulphonic acid as a catalyst (250 ml) for about 8 hours, and the benzene distilled off, until about 20 ml of solution remained. This was filtered, and the filtrate evaporated at room temperature under reduced pressure when the compound (56) crystallised out. The compound (56) was further purified by column chromatography, and by sublimation as described in the first procedure. Yield: 0.51g (40%).

The n.m.r. and the infra-red spectra of the compound (56) were as described in the first procedure.

7. Attempted Preparation of Cis-1,2-Dimethyl-Cyclohexa-3,5-Diene 1,2-Dicarboxylic Anhydride (56) from Cis-1,2-Dimethyl-4,5-Dibromo-Cyclohexane-1,2-Dicarboxylic Anhydride (58)

Cis-1,2-dimethyl-4,5-dibromo-cyclohexane-1,2-dicarboxylic anhydride (58) (100 mg), and 1,5-diaza-bicyclo (4,3,0) nona-5-ene (60) (1g) were dissolved in dry acetone (4 ml), and refluxed gently for about 8 hours.

The reaction mixture was extracted, as described in Section 5 (6), with a saturated solution of hydrogen chloride in dry ether.

The ether was removed from the extract, and the residue examined by thin layer chromatography, and infra-red spectrophotometry which indicated that an amount of the compound (56) had been formed. No further characterisation was made.

8. Attempted Preparation of Cyclobuta-1,3-Diene Iron Tricarbonyl (47)

Cyclobuta-1,3-diene iron tricarbonyl (47) was prepared from cis-3,4-dichloro-cyclobut-1-ene (50), and iron enneacarbonyl according to the procedure described by Pettit and co-workers.[28] The product was obtained as a viscous yellow oil.

The n.m.r. spectrum had (in pentane, reference, trimethyl silane) τ = 6.18 (H, singlet). (Literature, τ = 6.09, solvent unknown.)

The infra-red spectrum had carbonyl bands at ν_{max}: 2,100m, and at 1980s. (Literature, carbonyl bands at ν_{max}: 2055, and at 1985 cm^{-1}.)

9. Attempted Preparation of Tricyclo ($6,4,2,0^{1,6}$) Dec-3-Ene-2,5-Dione (209)

The compound, cyclobuta-1,3-diene iron tricarbonyl (47) (0.390g), and 1,4-benzoquinone (29) (0.5g) were dissolved in dry acetone (2 ml) at 0^{o}. Ceric ammonium nitrate (1.2g) was added in small increments, over a period of 1 hour.

The resulting mixture was filtered and the acetone removed from the filtrate. The infra-red spectrum of the residue was that of unchanged 1,4-benzoquinone (29).

10. Attempted Preparation of Dimethyl-Bicyclo ($2,2,0^{1,4}$) Hex-5-Ene 2,3-Dicarboxylate (49)

The compound, cyclobuta-1,3-diene iron tricarbonyl (47) (600 mg) and dimethyl maleate (16) (0.35g) were dissolved in anhydrous methanol at 0^{o}, and treated as described for the compound (209) in Section 5 (9) above. The infra-red spectrum of the residue was that of unchanged dimethyl maleate (16).

11. Preparation of 2,5-Dimethyl-3,4-Diphenyl-Cyclopentadiene-1-One Dimer (76)

This compound was prepared according to the method described by Gray.[34] Benzonitrile (80g), and diethylketone (60g) were added to a solution of potassium hydroxide (20g) in water (60 ml). Ethanol (2 ml) was added. The whole was stirred overnight with a Vibromix stirrer, then poured into hot water and allowed to cool, when solid material separated out. This was filtered off, and washed, first with warm water, and then with small amounts of ether to give a white waxy product (74g).

The product was added to a solution of acetic anhydride (20 ml) and concentrated sulphuric acid (3 ml) when it immediately dissolved to give a red-brown solution which on setting aside for a few minutes became green. The compound (76) separated out. It was filtered and washed first with water and then with ethanol (96%).

Recrystallisation from ethanol gave the compound, 2,5-dimethyl-3,4-diphenyl-cyclopentadiene-1-one dimer (76). Yield, 54g (39%), melting point 180^{o} (literature 180^{o}).

The infra-red spectrum had main bands at ν_{max}: 1768s, 1680s, 1600m, 1330m, 1015m, 810m, 790m, 770m, and at 695s cm^{-1}.

12. Preparation of Cis-3,4-Dichloro-1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-7-Ene-9-One (77)

2,5-dimethyl-3,4-diphenyl-cyclopentadiene-1-one dimer (76) (1.3g), and cis-1,2-dichloro-cyclobut-3-ene (50) (0.61g) were dissolved in benzene (15 ml), and refluxed gently for 48 hours. The solution was cooled, filtered, and concentrated by evaporation under reduced pressure. n-Hexane was added carefully, and a precipitate formed which was filtered off. Recrystallisation several times, from chloroform/n-hexane gave, cis-3,4-dichloro-1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one (77). Yield, 1g (52%), melting point 216°. (Found: C, 71.8; H, 5.5; O, 4.5; Cl, 15.5%. $C_{23}H_{20}O\,Cl_2$ requires C, 72.1; H, 5.3; O, 4.17; Cl, 18.5%.)

The n.m.r. had $\tau = 2.85 \pm 0.3$ (12H, multiplet, phenyl H), $\tau = 5.75$ (2H, multiplet, base = 7 cps, cyclobutyl H), $\tau = 7.04$ (2H, multiplet, base = 7 cps, cyclobutyl H), $\tau = 8.72$ (6H, singlet, methyl H).

The infra-red had main bands at ν_{max}: 1795w, 1765s, 1190m, 1080m, 920m, 900m, 875m, 820m, 780m, 765m, 725m, and at 705s cm^{-1}.

13. Preparation of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-One (80)

Cis-3,4-dichloro-1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one (77) (1g) was refluxed, with stirring, with activated zinc powder* (15g) in dry ethanol for 72 hours. The mixture was then evaporated to dryness, and extracted with ether. The ether extract was filtered, and the ether removed from the filtrate, by evaporation under reduced pressure, leaving a creamy-white residue.

Thin layer chromatography of the residue, in benzene on silica gel, showed only one mobile spot R_f 0.73 which did not correspond to the spot of the reference compound (77), R_f 0.33. Some material remained at the origin.

Thin layer chromatography using carbon tetrachloride as solvent showed a similar, but less mobile, pattern.

Chromatography of the residue on a silica gel column (50g) with benzene** as eluting solvent readily gave, 1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (80), which was

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* The zinc was activated by setting it aside in 10% ammonium chloride solution for 24 hours with occasional shaking.

** Carbon tetrachloride was also a good eluting solvent.

further purified by recrystallising it from ether. Yield, 0.6g (78%); melting point 126°. (Found: C, 88.0; H, 6.7; O, 5.9%. $C_{23}H_{20}O$ required C, 88.4; H, 6.5; O, 5.1%.)

The infra-red spectrum had main bands at ν_{max}: 1765s, 1280s, 1165m, 1070m, 1000m, 970m, 900m, 890m, 835s, 765m, 750s, 710s, and at 690s cm^{-1}.

The n.m.r. spectrum had τ = 2.86 ± 0.26 (12H, multiplet, aromatic H), τ = 3.47 (2H, apparent singlet, base = 4 cps, vinyl H), τ = 6.85 (2H, apparent singlet, base = 4 cps, tertiary H), and τ = 8.78 (6H, singlet, methyl H).

14. Preparation of N-Benzyl-1,6-Dimethyl-7,8-Diphenyl-Tricyclo (4,2,1,$O^{2,5}$) Nona-7-Ene-9-One 3,4-Dicarboximide (82)

2,5-dimethyl-3,4-diphenyl-cyclopentadiene-1-one dimer (76) (0.26g), and N-benzyl-cyclobut-3-ene 1,2-imide (83) (0.21g), were dissolved in benzene (5 ml), and gently refluxed for two days. The solution was then concentrated under reduced pressure. Pentane was added to the concentrated solution and a precipitate formed which was worked up, and filtered off.

Several recrystallisations from chloroform/n-hexane gave N-benzyl-1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one 3,4-dicarboximide (82). Yield, 0.32g (68%), melting point 228° (decomp). (Found: C, 79.4; H, 5.8; N, 2.9; O, 10.9%. $C_{32}H_{27}NO_3$ requires C, 81.2; H, 5.8; N, 3.0; O, 10.1%.)

The n.m.r. had τ = 2.85 ± 0.35 (18H, multiplet, phenyl H), τ = 5.28 (2H, singlet, methylene H), τ = 7.08 (2H, multiplet, base = 11 cps, cyclobutyl H), τ = 7.27 (2H, multiplet, base = 11 cps, cyclobutyl H), and τ = 8.68 (6H, singlet, methyl H).

The infra-red spectrum had main bands at ν_{max}: 1820w, 1770s, 1800s, 1350s, 1160s, 1075s, 820m, 760m, 740m, and at 700s cm^{-1}.

15. Preparation of the Adduct, Dimethyl-Tricyclo ($4,2,2,0^{2,5}$) Deca-3,7,9-Triene 7,8-Dicarboxylate (52)

The adduct of dimethyl acetylene dicarboxylate and cyclooctatetraene (69) was prepared according to Reppe.[19]

Dimethyl acetylene dicarboxylate (94) (7.1g 0.05M), and cyclooctatetraene (69) (5.2g 0.05M) were sealed in the Aminco High-Pressure Assembly and heated overnight at 160°.

The colourless, slightly odourous oil which was the compound, dimethyl-tricyclo (4,2,2,$0^{2,5}$) deca-3,7,9-triene 7,8-dicarboxylate (52) was obtained by repeated fractional vacuum distillation of the reaction mixture. It had an n.m.r. spectrum which had τ = 3.94 (4H, multiplet, vinyl H), τ = 6.21 (8H, singlet, with a multiplet around the base = 24 cps, methyl H, cyclobutyl H), and τ = 7.23 (2H, multiplet, tertiary H).

16. <u>Preparation of the Adduct, Dimethyl-4,7-Dimethyl-5,6-Diphenyl-Pentacyclo (8,2,2,$1^{4,7}$,$0^{2,9}$,$0^{3,8}$) Deca-5,11,13-Triene-15-One 11,12-Dicarboxylate (92)</u>

2,5-dimethyl-3,4-diphenyl cyclopentadiene-1-one dimer (76) (1.04g), and dimethyl-tricyclo (4,2,2,$0^{2,5}$) deca-3,7,9-ene 7,8-dicarboxylate (52) (0.98g), were dissolved in chloroform (15 ml) and refluxed gently for 30 hours.

The solution was evaporated down to give a viscous yellow liquid, still containing some solvent. The material was worked up, with the dropwise addition of n-hexane. A precipitate formed which was filtered off, dried, and recrystallised several times from diethyl ether to give small, white crystals of <u>dimethyl-4,7-dimethyl-5,6-</u>

diphenyl-pentacyclo ($8,2,2,1^{4,7},0^{2,9},0^{3,8}$) deca-5,11,13-triene-15-one 11,12-dicarboxylate (92). Yield, 0.77g (40%), melting point 185°. (Found: C, 77.8; H, 6.2; O, 15.9%. $C_{33}H_{30}O_5$ requires C, 78.2; H, 6.0; O, 15.8%.)

The infra-red spectrum had three carbonyl peaks ν_{max}^{nujol}: 1765s, 1745s, and 1710s with other main bands at ν_{max}^{nujol}: 1260s, 1205m, 1120m, 1110m, 1055s, 950m, 800m, 770m, 750s, 710s and at 690s cm^{-1}.

The n.m.r. spectrum had τ = 2.90 (10H, multiplet, aromatic H), τ = 3.48 (2H, triplet, base = 12 cps, vinyl H), τ = 5.90 (2H, multiplet, base = 16 cps, tertiary H), τ = 6.24 (6H, singlet, methoxyl H), τ = 7.92 and τ = 8.08 (each 2H, multiplet, common base = 18 cps, cyclobutyl H), and τ = 8.80 (6H, singlet, methyl H).

17. Preparation of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo-($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-One (80) by Pyrolysis of Dimethyl-4,7-Dimethyl-5,6-Diphenyl-Pentacyclo ($8,2,2,1^{4,7},0^{2,9},0^{3,8}$) Deca-5,11,13-Triene-15-One 11,12-Dicarboxylate (92)

The compound 1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (92) (1g) was heated at 190° for 15 minutes.

Thin layer chromatography examination of the pyrolysate on silica gel in chloroform, showed three spots with none corresponding to that of the original compound (92).

In chloroform the leading spot had an R_f 0.99, the next spot, an R_f 0.89 and the third spot, an R_f 0.17. The R_f of the reference compound (78) was 0.99 and of the reference compound (80) the R_f was 0.33.

The pyrolysate was taken up in carbon tetrachloride and run onto a silica gel column (25g). The column development was monitored by thin layer chromatography on silica gel. The column was first developed with carbon tetrachloride (25 ml × 12) eluted the compound corresponding to R_f 0.89. Evaporation of the solvent under reduced pressure gave compound (80). Yield, 150mg (80%).

Its n.m.r. had τ = 2.86 (10H, multiplet, aromatic H), τ = 3.47 (2H, singlet, vinyl H), τ = 6.85 (2H, singlet, tertiary H), and τ = 8.78 (6H, singlet, methyl H).

The infra-red spectrum of the compound (80) had main bands at ν_{max}: 1765s, 1280s, 965m, 1070m, 1000m, 970m, 900m, 890m, 840s, 770m, 750s, 710s, and at 690s cm^{-1}.

The first substance eluted from the column had an R_f 0.99, on silica gel in chloroform, which corresponded to that of reference compound (78). It was obtained in 20% (30mg) yield.

18. Preparation of Dimethyl-3,6-Dimethyl-4,5-Diphenyl-1,2-Phthalate (93)

2,5-dimethyl-3,4 diphenyl-cyclopentadien-1-one dimer (76) (0.65g), and dimethyl acetylene dicarboxylate (94) (0.31g) were dissolved in benzene (5 ml) and refluxed gently for 24 hours.

The cooled benzene solution was concentrated under reduced pressure when a separation of crystals occurred. These were filtered off and washed with ether. Recrystallisation several times from chloroform/n-pentane gave dimethyl-3,6-dimethyl-4,5-diphenyl-1,2-phthallate (93). Yield, 0.62g (65%), melting point 212°. (Found: C, 77.2; H, 6.2; O, 17.2%. $C_{24}H_{22}O_4$ requires C, 77.0; H, 5.9; O, 17.1%.)

The infra-red spectrum of the compound (93) had main bands at ν_{max}: 1730s, 1335s, 1205s, 1095m, 1025s, 925m, 810m, 770m, 720s, and at 690s cm^{-1}.

The n.m.r. spectrum had τ = 2.95 (10H, multiplet, 36 cps across base), τ = 6.08 (6H, singlet, methonyl H), and τ = 7.93 (6H, singlet, methyl H).

19. Attempted Preparation of the Adduct Dimethyl-4,7-Dimethyl-5,6-Diphenyl-Pentacyclo ($8,2,2,1^{4,7},0^{2,9},0^{3,8}$) Deca-5,11,13-Triene-15-One-11,12-Dicarboxylate (92)

2,5-Dimethyl-3,4-diphenyl-cyclopentadiene-1-one dimer (76) (1.25g), and dimethyl-tricyclo ($4,2,2,0^{2,5}$) deca-3,7,9-triene-7,8-dicarboxylate (52) (1.4g) were dissolved in benzene (10 ml) and refluxed for two days.

The solution was then concentrated by evaporation of the solvent, when crystals separated out. These were filtered off, and recrystallised several times from carbon tetrachloride/n-hexane to give dimethyl-3,6-dimethyl-4,5-diphenyl-1,2-phthalate (93). Yield, 10%, melting point 210°. The infra-red spectrum was identical with that of authentic (93), Section 5 (18).

20. Preparation of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-7-Ene-9-One-3,4-Dicarboxylic Anhydried (90)

3,4-Diphenyl-2,5-dimethyl-cyclopentadiene-1-one dimer (76) (1.30g), and cyclobut-3-ene-1,2-dicarboxylic anhydride (89) (0.62g)

were dissolved in benzene (15 ml), and refluxed gently for 12 hours under anhydrous condition. Crystals separated out, and were filtered off. The benzene filtrate was concentrated when more of the crystalline material separated out.

The compound 1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one-3,4-dicarboxylic anhydride (90) was recrystallised several times from benzene/n-hexane to give a yield, 1.16g (60%). Melting point 250°. (Found: C, 78.0; H, 5.3; O, 16.2%. $C_{25}H_{20}O_4$ requires C, 78.1; H, 5.2; O, 16.7%.)

The infra-red spectrum had main bands at ν_{max}: 1855w, 1780s, 1240s, 1215s, 1065s, 980m, 915s, 985m, and 710s cm^{-1}.

The n.m.r. spectrum had τ = 2.80 (12H, multiplet, aromatic H), τ = 6.85 (2H, singlet with slight splitting, base = 8 cps, cyclobutyl H), τ = 7.05 (2H, singlet with slight splitting, base = 8 cps, cyclobutyl H), and τ = 8.67 (6H, singlet, methyl H).

21. Attempted Preparation of 1,6-Dimethyl-3,4-Dimethyl 7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-7-Ene-9-One 3,4-Dicarboxylic Anhydride

2,5-Dimethyl-3,4-diphenyl cyclopentadiene-1-one dimer (76) (1.3g), and 1,2-dimethyl-cyclobut-3-ene-1,2-dicarboxylic anhydride (91) (0.32g), were dissolved in benzene (15 ml), and refluxed gently for 24 hours under anhydrous conditions.

The brown precipitate formed was filtered off. It appeared polymeric and was not characterised further.

The benzene was evaporated off from the filtrate and the residue upon examination consisted of compound (76) (1.3g) and a few mg of compound (91).

22. Preparation of Cis-3,4-Dichloro-Cyclobut-1-Ene (50)

Cis-3,4-dichloro-cyclobut-1-ene (50) was prepared from cyclooctatetraene (69) according to the procedure described by

Avram and co-workers,[64] in 40% yield, melting point 11° (literature, 11°). The infra-red spectrum had main absorptions at ν_{max}: 2960m, 1700w, 1290s, 1235s, 1190m, 1150s, 1110s, 1000m, 910s, 870m, 820s, and at 780s cm^{-1}.

The n.m.r. had τ = 3.71 (2H, apparent triplet, J = 1 cps, vinyl H), and τ = 4.84 (2H, apparent triplet, J = 1 cps, tertiary H).

23. Preparation of Dimethyl-4,5,6,7-Tetrachloro-15,15-Dimethoxy-Pentacyclo ($8,2,1^{4,7},0^{2,9},0^{3,8}$) Deca-5,11,13-Triene-15-One 11,12-Dicarboxylate (97)

1,2,3,4-tetrachloro-5,5-dimethoxy-cyclopenta-1,3-diene (98), (2.5g), and dimethyl tricyclo ($4,2,2,0^{2,5}$)-deca-3,7,9-triene 7,8-dicarboxylate (52) (2.14g) were dissolved in dry chloroform (120 ml), and refluxed gently for about 36 hours. The solution was then concentrated by evaporation of the chloroform under reduced pressure.

The resulting syrupy mass was worked up with the addition of n-hexane, until crystals separated out. These were filtered off, and washed with n-hexane.

Several recrystallisations from ether/n-hexane gave fine, white crystals of dimethyl-4,5,6,7-tetrachloro-15,15-dimethoxy-pentacyclo (8,2,1^{4,7},0^{2,9},0^{3,8}) deca-2,3,4,5-triene-15-one 11,12-dicarboxylate (97). Yield, 2.5g (54%), melting point 186^{o}. (Found: C, 49.4; H, 4.2; O, 17.6; Cl, 27.2%. $C_{21}H_{20}O_6Cl_4$ requires C, 49.4; H, 4.0; O, 18.2; Cl, 27.8%.)

The infra-red spectrum had main bands at ν_{max}: 1700s (ester), 1600m, 1270s, 1180m, 1060m, 1010m, 970m, 800s, 750s, and at 720s cm^{-1}.

The n.m.r. had τ = 3.39 (2H, triplet, base = 12 cps, vinyl H), τ = 5.89 (2H, multiplet, base = 18 cps, tertiary H), τ = 6.22 (6H, singlet, methoxy H), τ = 6.49 (6H, singlet, methoxyl H), τ = 2.63 (2H, multiplet, base = 12 cps, cyclobutyl H), and τ = 2.69 (2H, multiplet, base = 12 cps, cyclobutyl H).

A thin layer chromatogram of the compound (97) on silica gel in chloroform, gave a single spot, R_f 0.56.

24. Preparation of 1,6,7,8-Tetrachloro-9,9-Dimethoxy-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-One (96)

Dimethyl-4,5,6,7-tetrachloro-15,15-dimethoxy-pentacyclo ($8,2,2,1^{4,7},0^{2,9},0^{3,8}$) deca-5,11,13-triene-15-one 11,12-dicarboxylate (97) (1g) was heated for 15 minutes at 195-205° when pyrolysis took place. The pyrolysate was taken up in carbon tetrachloride, and developed in a silica gel column (40g) using carbon tetrachloride (25 ml × 16) for elution. The fractions eluting from the column were monitored by thin layer chromatography on silica gel, in chloroform. The substance corresponding to R_f 0.99 eluted readily.

The solvent was evaporated off carefully from the eluant under reduced pressure at 30°. Sublimation of the residue at 70°/0.5mm gave the white, waxy compound 1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (96). Yield, 0.64g (100%); melting point 80-81°. (Found: C, 42.1; H, 3.5; O, 9.7; Cl, 44.5%. $C_{11}H_{10}O_2Cl_4$ requires: C, 41.8; H, 3.2; O, 10.1; Cl, 44.9%.)

The infra-red spectrum had main bands at ν_{max}: 1600m, 1245s, 1175s, 1000s, 970s, 910m, 860m, 800s, 770s, and at 715 cm^{-1}.

The n.m.r. spectrum had τ = 3.97 (2H, singlet, vinyl H), τ = 6.41 (3H, singlet, methyl H), τ = 6.44 (3H, singlet, methyl H), and τ = 6.54 (2H, singlet, tertiary H, appearing to be slightly split).

25. Pyrolysis of 1,6,7,8-Tetrachloro-9,9-Dimethoxy-Tricyclo (4,2,1,$0^{2,5}$) Nona-3,7-Diene-9-One (110)

1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo (4,2,1,$0^{2,5}$) nona-3,7-diene-9-one (110) (36mg) was placed in a sealed tube under an atmosphere of nitrogen and heated at 200-210^{o} for 15 minutes, with slight yellowing.

The n.m.r. spectrum had τ = 6.44 (doublet, J = 1 cps, methoxy H, with multiplet around the base, tertiary H), and showed essentially unchanged compound (110).

The compound (110) was reheated to 280^{o} for 1 hour when some charring occurred with evolution of hydrogen chloride which was identified by (a) characteristic odour, (b) the vapour turned litmus-paper red, and (c) a silver nitrate solution became turbid.

After separation from the charred material the remainder of the pyrolysate had the same n.m.r. as the original compound (110).

26. Preparation of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-01 (118)

1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{3,5}$) nona-3,7-diene-9-one (80) (0.15g) and potassium borohydride (0.09g) were dissolved in dry ether (10 ml) and set aside, with occasional stirring, for 48 hours at room temperature.

The solvent was evaporated off under reduced pressure, the residue suspended in water and extracted with ether. The ether extract was dried with sodium sulphate, filtered, and the ether evaporated off to give white waxy crystals of 1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-ol (118). Yield, 0.15g (100%), melting point,

The infra-red spectrum had main bands at ν_{max}: 3650 m, 1665w, 1630w, 1605w, 1280m, 1130m, 1075s, 1050s, 850s, 775s, 760m, and at 695s cm^{-1}. The n.m.r. spectrum had τ = 3.98 (10H, multiplet, aromatic H), τ = 3.20 (2H, apparent singlet, base = 4 cps, vinyl H), τ = 6.91 (2H, apparent singlet, base = 6 cps, cyclobutyl H), and τ = 8.66 (6H, singlet, methyl H). Further the n.m.r. spectrum had τ = 6.7 (1H, multiplet, bridge-head H), and also τ = 6.5 (1H, broad, hydroxl H). With D_2O admixture τ = 6.5 disappears.

27. Preparation of the Adduct N-Benzyl-Bicyclo (4,2,0)-Octa-3-Ene 7,8-Imide (126)

N-benzyl-cyclobut-3-ene-1,2-dicarboximide (83) (0.73g) and buta-1,3-diene (124) (0.5g) in benzene (10 ml) were sealed in an Aminco High-Pressure Assembly under an initial atmosphere of nitrogen. The whole was shaken for 60 hours at 160° to 170°.

After cooling and release of slight pressure, the brown viscous material present was extracted with chloroform. Some unidentified polymeric material remained.

The filtered chloroform extract was chromatographed on a silica gel column (50g) with chloroform as eluant. On evaporation of the chloroform fractions, crystals formed readily, yield about 1.4g.

Recrystallisation from ether/n-hexane several times gave white, powdery crystals of the compound N-benzyl-bicyclo (4,2,0) octa-3-ene 7,8-dicarboximide (126). Yield, 0.3g (30%); melting point, 123°. (Found: C, 75.7; H, 6.4; O, 13.0; N, 5.1%. $C_{17}H_{17}O_2N$ requires C, 76.4; H, 6.4; O, 12.0; N, 5.2%.)

The n.m.r. spectrum had τ = 2.80 (5H, singlet, aromatic H), τ = 3.96 (2H, multiplet, vinyl H), τ = 5.34 (2H, singlet, methylene H),

τ = 7.30 (4H, singlet, a little broad at the base, cyclobutyl H), and τ = 7.80 (4H, multiplet, ring methylene H). The infra-red spectrum had main bands at ν_{max}: 1760m, 1695s (imide), 1430m, 1335s, 1280m, 1170s, 1140s, 1060m, 925s, 730s, 720s, and at 690s cm^{-1}.

The product (126) decolourised bromine/carbon tetrachloride solution.

28. Attempted Preparation of N-Benzyl-Bicyclo (4,2,0)-Octa-3,4-Dibromo 7,8-Dicarboximide

N-benzyl-bicyclo (4,2,0) octa-3-ene 7,8-dicarboximide (126) (0.2g) was dissolved in a mixture of acetic acid (3 ml), and chloroform (1 ml), and the solution cooled in an ice-bath. Bromine (200 mg) in chloroform (1 ml) was added to the mixture slowly, and in dropwise fashion. After an initial period of about 20 minutes the brown-red colour in the solution began to disappear. The mixture was left overnight.

The excess bromine, and the acetic acid was evaporated off under reduced pressure leaving a colourless, glassy solid which was soluble in chloroform.

A comparison of n.m.r. spectrum of this substance with that of compound (126) showed that the vinyl multiplet of (126) at τ = 3.96 had disappeared.

29. Attempted Preparation of Tricyclo ($4,2,2,0^{2,5}$) Deca-7-Ene-3,4,9,10-Dicarboxylic-3,4,9,10-Dicarboxylic Anhydride (128)

Cyclo-hexa-3,4-diene-1,2-dicarboxylic anhydride (127)* (0.6g), and cyclobut-3-ene-1,2-dicarboxylic anhydride (89) (0.5g) were dissolved in dry benzene (15 ml), and refluxed gently overnight under anhydrous conditions. Crystals separated out from the solution were filtered off, and washed with benzene. (Yield, about 100mg.) The infra-red spectrum had main bands at ν_{max}: 1850m, 1770s, 1690s, 1310w, 1230s, 1190w, 1080s, 950w, 920s, 810w, 750m, and 680m cm^{-1}. Attempts to purify the compound (128) by recrystallisation resulted in its loss.

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* Supplied by Dr. J.B. Bremner of this Department.

The infra-red spectrum of an authentic sample of an analogous compound (129)** had main bands at ν_{max}: 1850m, 1770s, 1250s, 1230s, 1190m, 1075s, 950m, 910s, 810m, 750m, and at 680m cm^{-1}.

30. Preparation of N-Benzyl-Maleimide (84)

N-benzyl-maleimide (84) was prepared according to the procedure described by Mehta and co-workers.[82] Melting point 91-92° (literature 93°).

The n.m.r. spectrum had τ = 2.68 (5H, singlet, base = 16 cps, aromatic H), τ = 3.30 (2H, singlet, vinyl H), and τ = 6.32 (2H, singlet, methylene H).

** Supplied by Dr. R.N. Warrener of this Department.

31. Preparation of N-Benzyl Citraconimide (181)

Citraconic anhydride (34) (7.9g), and redistilled benzylamine (182) (7.5g) were dissolved in 2-ethoxyethanol (20 ml), and heated overnight on a water bath. (Precautions were taken to exclude carbon dioxide.)

The resulting light-brown solution was poured into water (200 ml), and the mixture extracted with ether. The ether extract was dried with sodium sulphate, filtered, and the ether evaporated off.

The viscous liquid remaining was then distilled under vacuum, 129-130° (vapour), 150-160° (bath)/0.5mm, to give N-benzyl citraconimide (181). Yield, 11g (64%); melting point 27-28° (literature 29°).

The infra-red spectrum (liquid film) had main bands at ν_{max}: 1770w, 1710s, 1640w, 1440s, 1400s, 1350s, 1120m, 1060m, 950s, 860s, 765m, 710s, and at 690s cm^{-1}.

The n.m.r. spectrum had τ = 2.73 (6H, singlet, phenyl H), τ = 3.7 (1H, apparent doublet, J = 2-3 c/s, vinyl H), τ = 5.35 (2H, singlet, methylene H), and τ = 7.94 (3H, doublet, J = 2-3 c/s, methyl H).

32. Preparation of 2-Methyl-1,4-Naphthoquinone Dimer (3)

2-methyl-1,4-naphthoquinone (1) (4g), was spread thinly in Petrie dishes, and irradiated, with periodic mixing for 6 weeks by a battery of four General Electric Black-light lamps (F158, BLB).

Thin layer chromatography on silica gel using the solvent systems, benzene, chloroform, and ethanol/chloroform (1:9 by volume), in each case showed only two mobile spots, one of which had an Rf corresponding to that of authentic (1).

The irradiated material was washed with small amounts of ether, and then recrystallised several times from ethanol to give 2-methyl-1,4-naphthoquinone dimer (3), in 90% yield. Melting point, 234° (literature 235°). (Found: C, 76.9; H, 4.7%. Calculated for $C_{22}H_{16}O_4$: C, 76.7; H, 4.7; O, 18.6%.)

The infra-red spectrum showed main bands at ν_{max}: 1840w, 1775m, 1690s, 1595s, 1300s, 1265s, 940m, 750s, and at 710 cm^{-1}.

The n.m.r. had τ = 2.36 (8H, multiplet, base = 30 cps, aromatic H), τ = 6.16 (2H, singlet, cyclobutyl H), and τ = 8.40 (6H, singlet, methyl H).

33. Preparation of 5-Methyl-2-Isopropyl-Benzoquinone (183)

5-methyl-2-isopropyl-benzoquinone (183) was prepared from 5-methyl-2-isopropyl phenol (184) according to the procedure described by Kremers and co-workers.[63] Melting point 44° (literature 45.5°).

The n.m.r. spectrum had τ = 3.42 (1H, apparent doublet, J = 1 cps, vinyl H), τ = 3.40 (1H, multiplet, base = 6 cps, vinyl H), τ = 6.96 (1H, multiplet, base = 33 cps, J = 8 cps, tertiary H), τ = 8.18 (3H, doublet, J = 1 cps, methyl H), and τ = 8.88 (6H, doublet, J = 8 cps, methyl H).

34. Photolysis (General)

With the exception of the studies using acetylene, all the photolyses were carried out in a water-cooled immersion-type photochemical reactor, such as that illustrated in Plate 1.

The essential parts of this reactor are illustrated in Plate 2. The numbers used in the following description are indicated on these plates.

The ultraviolet lamp, in this case an Hanovia U.V.S. 500 watt high-pressure, mercury arc-lamp (1) was placed inside a filter sleeve (2) which was inserted within the water-cooled quartz probe. The complete probe assembly was then fitted into the outer pyrex jacket (4) which contained the solution to be photolysed.

The solution could be stirred magnetically, and by a gas-lift circulator (6). The gas used in this circulation was either dry argon (water: 25 p.p.m; oxygen ca 0.2% removed by bubbling the gas through an alkaline pyrogallol solution).* These gases also maintained an inert atmosphere during the photolyses.

Samples of the reaction mixture were obtained from the sampling inlet (5), without stopping the photolysis. Solvent

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* These gas analyses are according to the Commonwealth Industrial Gases Limited, Sydney, N.S.W.

PLATE 1

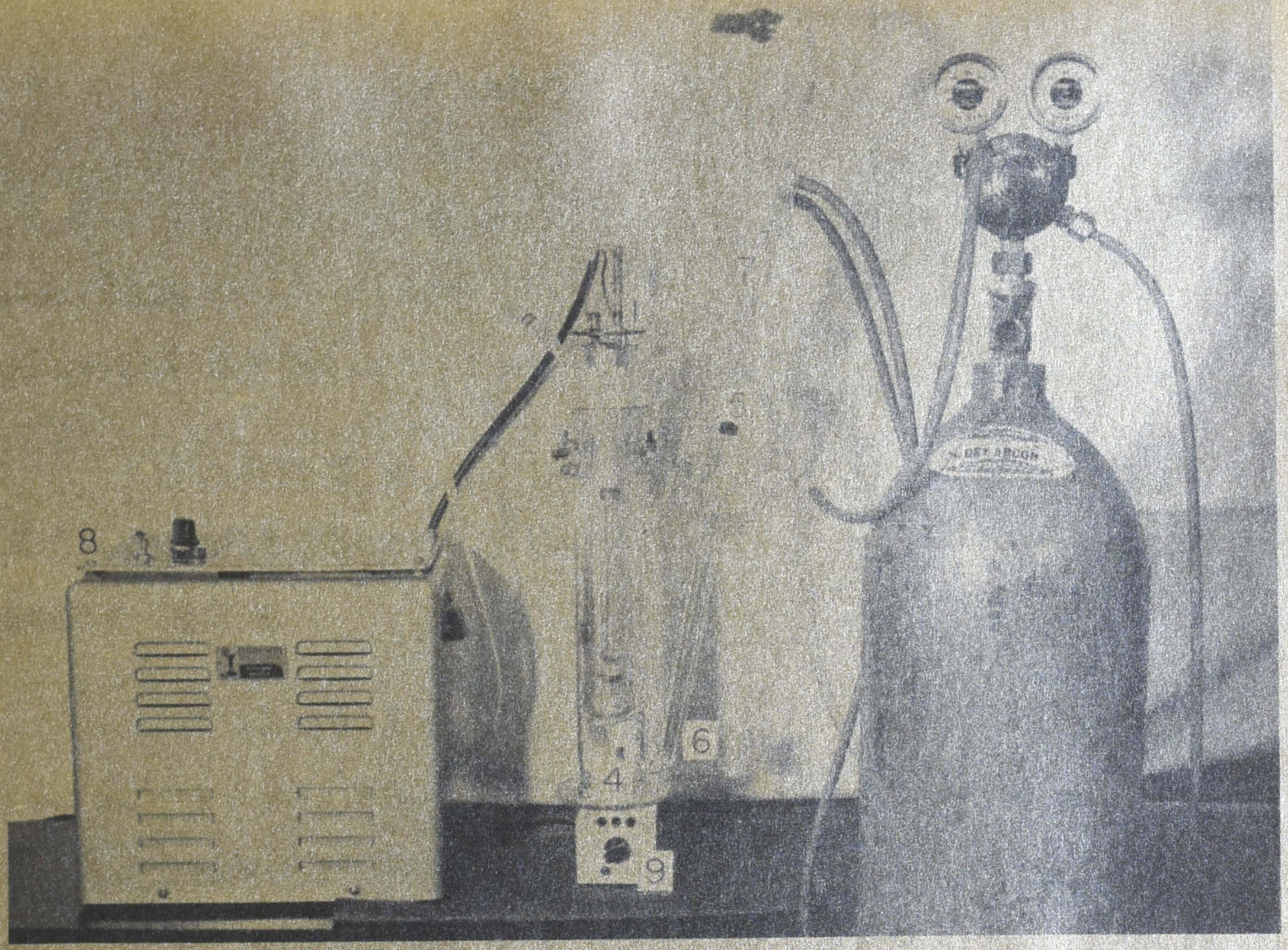
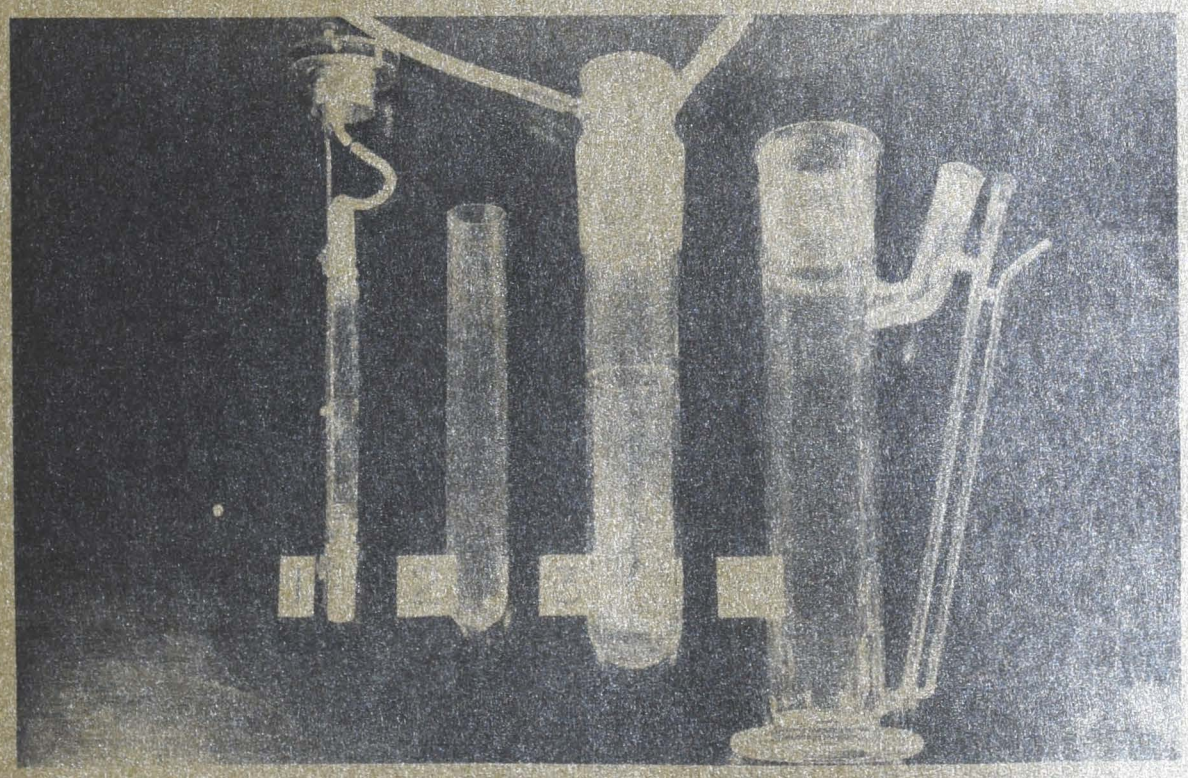


PLATE 2



evaporation was minimised by the use of a water cooled condenser (D). A drying tube was fitted to the condenser.

There were two pyrex outer jackets, one which allowed for the photolysis of 230 ml of solution and one which allowed for the photolysis of 1000ml of solution.

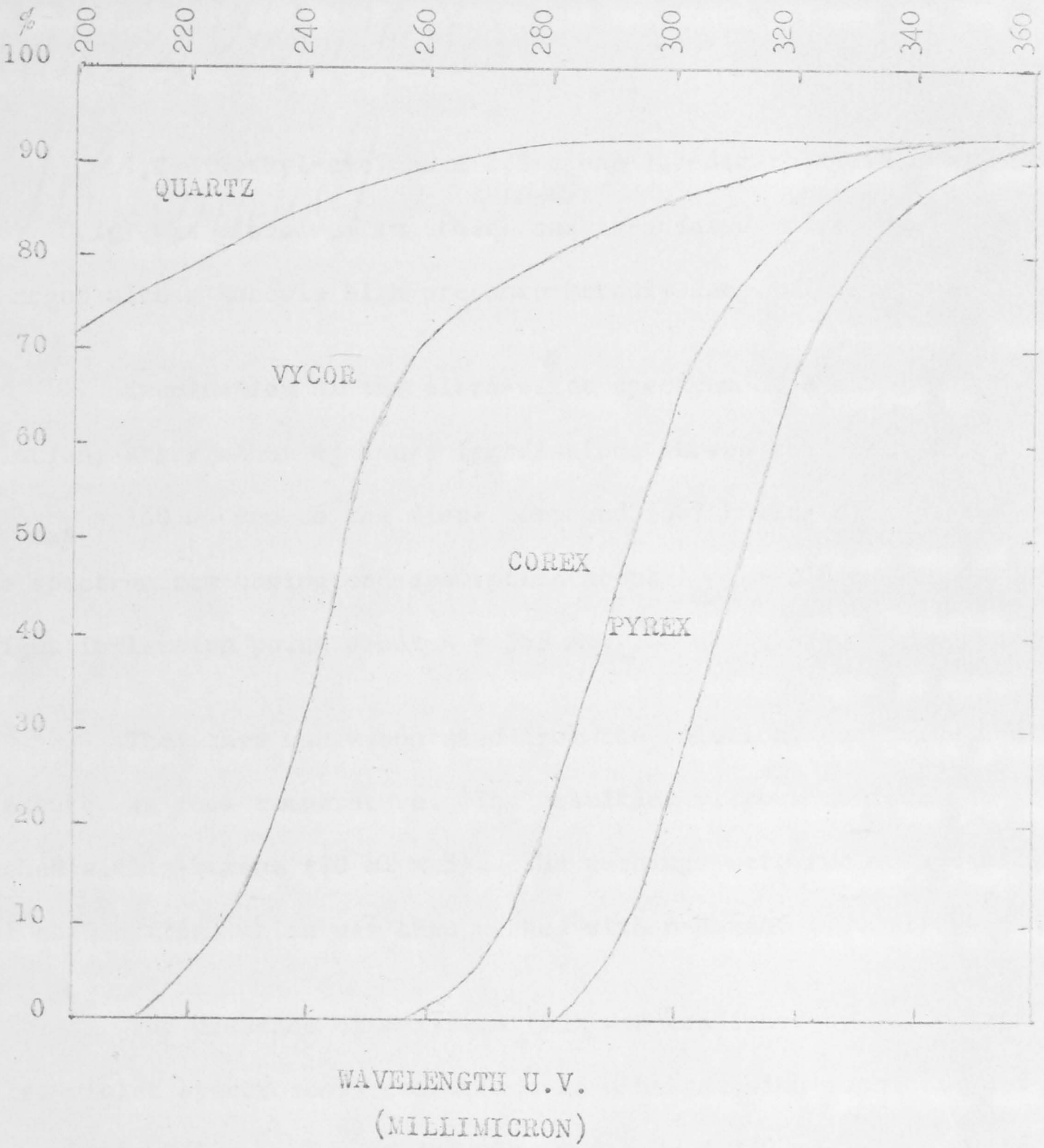
For the photolysis of ether, or acetone solutions, the whole apparatus was placed in an ice bath.

Another ultraviolet lamp was used in some photolyses. This was the Hanau medium-pressure mercury lamp, NK G/20, supplied by Quarz Lampen Gesellschaft m.b.H., Hanau, Germany.

Three different types of filter sleeve were used, one of Vycor glass, from Engelhard Industries Inc., Hanovia Lamp Division, New Jersey, U.S.A., and which transmits ultra-violet light of wavelength greater than 210 mμ ; another filter sleeve was of Corex glass which transmits ultra-violet light of wave length greater than 260 mμ . The remaining filter sleeve was made of Pyrex which transmits light of wavelength greater than 280 mμ . The spectral characteristics of these filters are shown in Diagram 37.

All the solvents used in the photolyses were purified, and dried before being used.

DIAGRAM 37



WAVELENGTH U.V.
(MILLIMICRON)

35. Photolysis of 1,2-Dimethyl-Cyclohexa-3,5-Diene-1,2 Dicarboxylic Anhydride (56)

1,2-dimethyl-cyclohexa-3,5-diene-1,2-dicarboxylic anhydride (56) (0.7g) was dissolved in ether (230 ml), and irradiated under an atmosphere of argon with a Hanovia high pressure mercury lamp.

Examination of the ultra-violet spectrum of a sample of the solution, after about $4\frac{1}{2}$ hours irradiation, showed that the absorption at λ_{max} = 260 mμ due to the diene compound (56) having disappeared and the spectrum now having end-absorption about λ_{max} = 218 mμ, and a slight inflection point about λ = 265 mμ .

The ether was evaporated from the solution, under reduced pressure, at room temperature. The resulting viscous residue was washed with n-hexane (10 ml × 3). The washings were run onto a silica gel column (25g) which was then washed with n-hexane (100 ml).

The presence of o-xylene (65) was confirmed by quantitative ultra-violet spectroscopy comparison in n-hexane with authentic o-xylene, λ_{max} = 264, 272 mμ , $\lambda_{I/P}$ = 268 mμ , and λ_{min} = 270 mμ . Yield, 157 mg (38%).

The substance remaining, was then taken up in a little benzene/n-hexane solution (1:3 by volume), and run onto the column which was

developed with benzene/n-hexane solution (1:3 by volume) (24 ml × 21).

The progress of development was monitored by thin layer chromatography on silica gel in benzene. The olefinic compound (57) began to appear after eluting solution (25 ml × 11) had been passed through the column. The two valence isomers (66) and (67), of 5,6-dimethyl-bicyclo (2,2,$0^{1,4}$) hex-5-ene 5,6-dicarboxylate were next to elute from the column. Development of the column was complete when elution solution (25 ml × 21) had passed through.

None of the three compounds was obtained free from the others. Total, collective yield was 70 mg (10%). The mixture was sublimed at 35°/0.5mm. Analysis of the mixture was: Found: C,66.6, H, 5.8%.

The infra-red spectra of the substances from the four relevant fractions had main bands as tabulated:

ν_{max} =	Reference Olefine (57)	Column Fraction			
		14	15	16	17
cm^{-1}	1840m	1840m	1840m	1840m	1840m
"	1770s	1770s	1770s	1770s	1770s
"	1285m	1285w		1285w	
"	1260m	1260m	1260m	1260w	
"	1220s	1220s	1220m	1220m	1220m
"	1190w	1190s	1190m		
"			1180m	1180m	1180m
"	1100w	1100m	1100m	1100m	
"	1000s	1000s	1000m	1000m	
"	980s	980s	980m	980m	
"			970s	970s	970s
"	910m	910m	910m		
"		900m	900s	900s	900s
"			870w	870m	870w
"				840w	840w
"				790w	790w
"			775m	775w	
"	750m	750w			
"		710m	710m	710s	710s
"	690s	690m	690w	690w	

The n.m.r. of spectra of the relevant column fractions had signals as tabulated at τ =

τ =	Reference Olefine (57)	Column Fraction		
		14	16	17
multiplet, vinyl H		3.54	3.58	3.52
" " "	4.08	4.04	4.05*	4.1**
" " "		6.50	6.50*	6.51**
" " "		6.70	6.70	6.75
" " "	3.2	7.14	7.20*	
" " "	7.45	7.44	7.43*	
" " "	7.88	7.84	7.82*	
" " "	8.01	8.14	8.10*	
singlet, methyl H		8.57^{3}	8.55^{1}	$8.60s^{1}$
" " "	8.64	8.63^{1}	8.61^{2}	8.65^{3*}
" " "		8.73^{2}	8.71^{2}	8.74^{2*}

* Decreasing in signal by inspection of spectra;

** Signal trace only, by inspection of spectra;

Superscripts 1,2 and 3 indicate decreasing relative order of signal intensities.

A portion (30mg) of the anhydride mixture was heated in a sealed tube at 200° for 10 minutes. The n.m.r. spectrum showed unchanged signals for compound (57) at τ = 4.04, 7.14, 7.44, 7.84, and 8.63 respectively with further signals at τ = 3.9 (multiplet, vinyl H), τ = 4.26 (multiplet, vinyl H), and τ = 8.62 (singlet, methyl H). This latter group of n.m.r. signals corresponded to those of the compound (56).

36. Photolysis of Cis-3,4-Dichloro-1,6-Dimethyl-7,8-Diphenyl-Tricyclo (4,2,1,$0^{2,5}$) Nona-7-Ene-9-One (77)

Cis-3,4-dichloro-1,6-dimethyl-7,8-diphenyl-tricyclo (4,2,1,$0^{2,5}$) nona-7-ene-9-one (77) (400mg) was dissolved in anhydrous ether (230 ml), and irradiated under an atomsphere of argon, with a Hanau medium-pressure lamp, using a Vycor filter. Samples were taken from the solution, and examined by thin layer chromatography on silica gel, in carbon tetrachloride. This showed that after about eight hours irradiation, the compound (77) had disappeared (R_f 0.33), and a new mobile spot had appeared at R_f 0.86.

The etheral solution was evaporated down under reduced pressure, and the residue chromatographed on a silica gel column

(20g), using ether/n-hexane (1:19 volume by volume) as eluant (25 ml × 11). The column was monitored by the thin layer chromatography system described above. The compound corresponding to the mobile spot R_f 0.86 was isolated in the first six fractions.

Recrystallisation from carbon tetrachloride, and sublimation at 70°/0.5mm gave 1,4-dimethyl-2,3-diphenyl benzene (78). Yield, 69%; melting point 89-90°. (Found: C, 92.5; H, 7.1; Calculated for $C_{20}H_{19}$: C, 93.0; H, 7.0%.)

The n.m.r. spectrum had τ = 2.97 (8H, multiplet, aromatic H), τ = 7.93 (6H, singlet, methyl H). The infra-red spectrum had main bands at ν_{max}: 1600m, 1080m, 1035m, 920m, 815m, 765s, 735m, and at 705s cm^{-1}. The characteristics were identical with those of an authentic sample (78).*

Nothing further was eluted from the column with continual development and finally the column was washed with ether (200 ml). The brown amorphous residue left after evaporation of the ether from the ethereal solution gave a strongly positive Bielstein-Marsh Test for chloride.

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* Supplied by Dr. Bremner of this Department.

37. Photolysis of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-One (80) in Ether

First Procedure

1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (80) (511mg) was irradiated in ether according to the procedure described for compound (77) and using the Hanau medium-pressure lamp. Samples were taken from the solution and examined by thin layer chromatography on silica gel in carbon tetrachloride. This showed that after about eight hours the compound (80) had disappeared (reference compound (80) spot R_f 0.33), and that a new mobile spot R_f 0.89 had appeared which corresponded to the R_f 0.89 of the compound (78) reference spot.

After evaporation of the solvent from the reaction mixture, the residue obtained was chromatographed on a silica gel column (20g), using carbon tetrachloride (25 ml × 11) as eluant. The thin layer chromatographic system, described above, was used to monitor the column development, the aromatic compound (78) eluted readily.

Recrystallisation from carbon tetrachloride gave the compound (78) in 56% yield. It was identified by the infra-red

spectrum which had main bands at ν_{max} : 1600m, 1080m, 1035m, 920m, 815m, 765s, 735m, and at 705s cm^{-1}.

Second Procedure

1,6-dimethyl-7,8-diphenyl-tricyclo (4,2,1,$0^{2,5}$) nona-3,7-diene-9-one (80) (370mg) was irradiated in ether in the manner previously described in Section 5(36)using a Pyrex filter.

Periodic monitoring of samples of the irradiated solution with thin layer chromatography, on silica gel in carbon tetrachloride, showed the slow appearance of a compound with an R_f 0.89 corresponding to that of reference aromatic compound (78). The only other mobile spot had an R_f 0.37 which corresponded to that of reference compound (80).

Irradiation was stopped after about 31 hours, and the solvent evaporated from the solution. The residue obtained was chromatographed on silica gel column (25g) using carbon tetrachloride as eluant.

The aromatic compound (78) was eluted from the column, first, 85 mg (28%) yield. As development proceeded the compound (80) was eluted in 250 mg (68%) yield.

38. Photolysis of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$)-Nona-3,7-Diene-9-One (80) in Acetone

1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$)-nona-3,7-diene-9-one (80) (1mg) was dissolved in acetone (230 ml) and irradiated under the conditions described for compound (80), Section 5(37) for two hours.

A sample of the solution was examined by thin layer chromatography on silica gel in carbon tetrachloride. A single mobile spot R_f 0.8 was observed, with material remaining at the origin. Reference aromatic compound (78) had a similar R_f 0.8. There was no spot present corresponding to the reference compound (80) R_f 0.2.

A further thin layer chromatogram on silica gel in n-hexane gave two mobile spots at R_f 0.4 and R_f 0.25 which corresponded respectively with that of reference compound diphenyl acetylene (81) R_f 0.4 (characteristic orange red-spot with ceric sulphate spray), and reference aromatic compound (78).

The acetone was evaporated off under reduced pressure and the residue obtained was chromatographed on a silica gel column (20g) using carbon tetrachloride as eluant (25 ml × 8). A mixture of

diphenyl acetylene (81) and aromatic compound (78) was obtained. Yield, 37mg (37%). U.V. spectroscopy of the mixture confirmed the presence of (81) by comparison with the U.V. spectrum of authentic (81). The U.V. spectrum had absorptions at λ_{max}: 273, 280, 288 and 297 mμ ; λ_{min}: 276, 286 and 293 mμ .

After further development of the column, the carbon tetrachloride eluant was concentrated by evaporation under reduced pressure. An n.m.r. spectrum of the solution had τ = 2.73 (singlet, with broadening at the base, aromatic H), and τ = 7.79 (singlet, methyl H) which was similar to the n.m.r. spectrum of authentic o-xylene (65).

39. Irradiation of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-One (80) by Sunlight

1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (80) (100mg) was crystallised in a thin layer on the inside of a silica tube, and irradiated for three weeks under a nitrogen atmosphere, in sunlight.

An examination by n.m.r. of the irradiated material after this time showed it to be unchanged (80).

40. Photolysis of N-Benzyl-1,6-Dimethyl-7,8-Diphenyl-Tricyclo (4,2,1,$0^{2,5}$) Nona-7-Ene-9-One 3,4-Dicarboximide (82)

N-benzyl-1,6-dimethyl-7,8-diphenyl-tricyclo (4,2,1,$0^{2,5}$) nona-7-ene-9-one-3,4-dicarboximide (82) (100mg) was dissolved in acetone (230ml), and irradiated for about $6\frac{1}{2}$ hours, using a Hanau medium-pressure lamp with a Vycor filter.

The solvent was evaporated, under reduced pressure, from the solution and the residue chromatographed on a silica gel column (20g). Ether/n-hexane (1:9 by volume) (25 ml × 12) eluted the aromatic compound (78) in 94% yield. The compound (78) was identified by thin layer chromatography on silica gel in carbon tetrachloride, with an R_f 0.78 similar to that of reference compound (78) R_f 0.78. Also, the infra-red spectrum had main bands at ν_{max}: 1600m, 1080m, 1035m, 920m, 815m, 765s, 735m, and at 705s cm^{-1} similar to those of authentic (78).

Further development of the column with ether/n-hexane, 1:4 by volume (25 ml × 5), eluted N-benzyl-maleimide (84), which was identified by thin layer chromatography on silica gel using ether/n-hexane (1:1 by volume). An R_f 0.5 was obtained corresponding to

that of reference N-benzyl-maleimide (84). Further, the infra-red spectrum had main bands at ν_{max}: 1765w and at 1700s (imide). It was found impossible to purify the N-benzyl maleimide (84) obtained from the photolysis.

41. Photolysis of 1,6,7,8-Tetrachloro-9,9-Dimethoxy-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-One (96) in Ether

The compound 1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (96) (250mg) was dissolved in dry ether (230 ml) and irradiated, under an atmosphere of argon, with a Hanovia high-pressure lamp, using a Vycor filter.

A sample of the solution, after four hours irradiation, was examined by thin layer chromatography on silica gel, in carbon tetrachloride. A single mobile spot R_f 0.52 was present, and also streaking from the origin to R_f 0.25. There was no spot corresponding to reference compound (96) R_f 0.75.

The ether was evaporated from the solution, under reduced pressure, and the syrupy residue obtained taken up in carbon tetrachloride, and run onto a silica gel column (15g). The column

development was monitored by thin layer chromatography on silica gel in carbon tetrachloride (16 × 25 ml) until all the material corresponding to the thin layer R_f 052 had been eluted.

The solvent was evaporated off to give a colourless oil (99) of 74% (184mg) yield.

The n.m.r. had τ = 4.03 (singlet, vinyl H), τ = 4.18 (singlet, vinyl H), τ = 6.39 (singlet, methoxy H), τ = 6.42 (singlet, methoxy H), and τ = 6.56 (singlet with slight splitting, tertiary H). The methoxy H signals and the tertiary H signals arose sharply from a broad base, 30 cps about τ = 6.40 (apparent multiplet). The ratio of peak integration was 1:1:12.3 respectively. The infra-red spectrum (liquid film) had main bands at ν_{max}: 1460m, 1230s, 1180s, 1090s, 970m, 930m, 830m, and 780s cm^{-1}.

The column was further developed with chloroform 50%/carbon tetrachloride 50% (25 ml × 9) to give a thick yellow oil (100mg). The n.m.r. spectrum had broad (36 cps) signals at τ = 6.45 and τ = 8.83. The infra-red spectrum (liquid film) had broad main bands at ν_{max}: 1730m, and 1100s cm^{-1}.

The residue gave a strong Bielstein-Marsh Test for chlorine.

Finally, washing the column with ether gave a yellow-brown oil which did not give any τ-values when examined by n.m.r.

42. Photolysis of 1,6,7,8-Tetrachloro-9,9-Dimethoxy-Tricyclo (4,2,1,$0^{2,5}$) Nona-3,7-Diene-9-One (96) in Acetone

1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo (4,2,1,$0^{2,5}$) nona-3,7-diene-9-one (96) (222mg) was dissolved in acetone (230 ml) and irradiated under the conditions described in Section 5(41) above.

A sample of the solution, after four hours irradiation, was examined by thin layer chromatography on silica gel in carbon tetrachloride. A single mobile spot R_f 0.24 was present, with material remaining at the origin. There was no spot corresponding to reference compound (96) R_f 0.8.

The acetone was evaporated from the solution, and the residue obtained, taken up in carbon tetrachloride and run onto a silica gel column (20g). The substance corresponding to thin layer R_f 0.24 eluted readily, and after recrystallisation from carbon tetrachloride, and sublimation at 90^{o}/0.5mm gave 2,3,5,6-tetra-chloro-4,4-dimethoxy-pentacyclo (5,2,0,$0^{2,3}$,$0^{5,6}$,$0^{8,9}$) nonane (110). Yield, 213mg (96%); melting point 123^{o}. (Found: C, 42.1; H, 3.4; 0, 10.1; Cl, 43.7%. $C_{11}H_{10}O_2Cl_4$ requires: C, 41.8; H, 3.2; 0, 10.1; 44.9%.)

The n.m.r. had τ = 6.44 (doublet, J = 0.1 cps, methoxy H), with multiplet at the base, over range of τ = 6.23 to τ = 6.53

(18 cps), tertiary H. The infra-red had main bands at ν_{max}: 1225s, 1175m, 1145m, 1090s, 1030m, 985m, 930m, 910w, 800s, and at 780s cm^{-1}.

43. Photolysis of 1,6,7,8-Tetrachloro-9-Dimethoxy-Tricyclo (4,2,1,$0^{2,5}$) Nona-3,7-Diene-9-One (96) in Carbon Tetrachloride

1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo (4,2,1,$0^{3,5}$) nona-3,7-diene-9-one (96) (200mg) and benzophenone (111) (0.8g) were dissolved in dry carbon tetrachloride (230ml) and irradiated under the conditions described in Section 5(41) above.

A sample of the solution, after four hours irradiation, was examined by thin layer chromatography on silica gel in carbon tetrachloride. There was no spot present corresponding to that of the reference compound (96) R_f 0.73. There were two overlapping spots present at R_f 0.38 and R_f 0.33. The reference compound (110) had an R_f 0.38 and reference benzophenone (111) had R_f 0.33.

The carbon tetrachloride was evaporated from the solution, and the yellow-brown residue obtained was chromatographed on silica gel column (30g) using carbon tetrachloride as eluant. Benzophenone

(111) and the compound 1,6,7,8-tetrachloro-9,9-dimethoxy-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-one (110) eluted together.

Repeated chromatography, and finally sublimation of the mixture, first at room temperature/0.5mm, and then at 90°/0.5mm reduced the amount of benzophenone (111) contaminating the compound (110).

The n.m.r. had τ = 6.40 (doublet, J = 1 cps, methoxy H), with multiplet (tertiary H) around the base, and τ = 2.40 (multiplet, aromatic H). The n.m.r. of benzophenone has τ = 2.4 (multiplet, phenyl H).

43. Photolysis of 1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-3,7-Diene-9-Ol (118)

1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-3,7-diene-9-ol (118) (0.15g) was dissolved in dry acetone (230 ml), and irradiated for about $3\frac{1}{2}$ hours according to the procedure described for the compound (96), Section 5(42).

A thin layer chromatogram, of the solution on silica gel in chloroform showed a mobile spot R_f 0.55, which corresponded to the reference compound (118) R_f 0.55, and streaking at the origin to R_f 0.14.

The acetone was evaporated off from the solution, and the residue obtained was chromatographed on a silica gel column (10g) using chloroform as eluant. The compound (118) was recovered predominantly unchanged, according to its n.m.r. spectral characteristics.

44. Photolysis of Dimethyl-4,7-Dimethyl-5,6-Diphenyl-Pentacyclo ($8,2,2,1^{4,7},0^{2,9},0^{3,8}$) Deca-5,11,13-Triene-15-One 11,12-Dicarboxylate (92)

Dimethyl-4,7-dimethyl-5,6-diphenyl-pentacyclo ($8,2,2,1^{4,7}$, $0^{2,9},0^{3,8}$) deca-5,11,13-triene-15-one 11,12-dicarboxylate (92) (1.1g) was dissolved in ether (230 ml), and irradiated, under argon, using a Hanovia high-pressure mercury lamp with a Corex-glass filter.

Samples were removed periodically from the solution and examined by thin layer chromatography on silica gel in chloroform, until the compound (92) had disappeared at about 17 hours, as evidenced by there being no thin layer spot corresponding to reference compound (92), R_f 0.33. Two new mobile spots had appeared, one running practically with the solvent front, and the other a diffuse spot at R_f 0.5.

The ether was evaporated off from the solution under reduced pressure at room temperature.

The residue obtained was adsorbed onto silica gel, and placed on the top of a silica gel column (50g). The chromatographic column was developed first with carbon tetrachloride/n-hexane (1:1 by volume) (20 ml × 15) without any elution of products.

Carbon tetrachloride (20 ml × 15) was then passed through the column, and the aromatic compound (78) was obtained. Yield, 290mg (52% Th). The thin layer chromatogram on silica gel in carbon tetrachloride of the eluted compound (78) corresponded to that of reference aromatic compound (78); the n.m.r. spectrum had τ = 2.97 (12H, multiplet, aromatic H), and τ = 7.93 (6H, singlet, methyl H).

Ether/carbon tetrachloride (1:95 by volume) (20 ml × 20) next eluted from the column, material corresponding to the thin layer R_f 0.5. Recrystallisation from ether gave a white solid (185). Yield, 117mg (11% w/w), melting point 220°. (Found: C, 79.1; H, 6.2; O, 13.9%.)

The n.m.r. spectrum had τ = 2.97 (multiplet, base = 33 cps, aromatic H), τ = 3.89 (multiplet, base = 9 cps, vinyl H), τ = 4.07 (multiplet, base = 9 cps, vinyl H), τ = 5.87 (multiplet, base = 9 cps), τ = 6.20 (singlet, methoxyl H), τ = 6.26 (singlet, methoxyl H), τ = 6.48 (multiplet, base = 11cps), τ = 7.95 (singlet, methyl H), and τ = 8.30 (singlet, methyl H).

The infra-red spectrum had main bands at ν_{max} (carbon disulphide): 1730s, 1270s, 1215m, 1070m, 745m, and at 690 cm^{-1}.

The column was further developed with ether/carbon tetrachloride (20 ml × 10) to give a semisolid substance which on recrystallisation from ether gave a white solid (186). Yield, 60mg (5% w/w), melting point 197-198°. (Found: C, 74.0; H, 6.1; O, 18.6%.)

The n.m.r. spectrum had τ = 3.02 (multiplet, aromatic H), τ = 3.36 (multiplet, base = 12 cps, vinyl H), τ = 5.82 (multiplet, base = 16 cps, tertiary H), τ = 6.18 (singlet, methoxy H), τ = 7.7 (multiplet, base = 12 cps, cyclobutyl H), τ = 7.87 (multiplet, base = 12 cps, cyclobutyl H), and τ = 8.97 (singlet, methyl H). The ratio of the peak integrations was: 5.75:1:1:3:1:1:3 respectively.

The infra-red spectrum had main bands ν_{max} (carbon disulphide): 1715s, 1260s, 1210w, 1130m, 1060s, 960m, 730m, and at 690 cm^{-1}.

The yellow-coloured ethereal mother-liquor from the crystallisation of the substance (186) was treated with pentane to give a fluffy white substance (197). Yield, 524mg (48%), melting point range: 115-127°. The n.m.r. spectrum had no distinguishable characteristics. The infra-red spectrum had main bands at ν_{max}: 1730s (broad), 1270m (broad), and at 730m (broad) cm^{-1}.

The ultraviolet spectrum showed end-absorption λ_{max} = 220 mμ, an inflection point at $\lambda_{I/P}$ = 250 mμ, and an inflection point at $\lambda_{I/P}$ = 330 mμ. $E_{1\%,\ 1cm}$, λ_{220} = 434; $E_{1\%,\ 1cm}$, λ_{220} = 353, and $E_{1\%,\ 1cm}$, λ_{330} = 52.

The solvent was evaporated from the filtrate of (187) under reduced pressure, and the residue extracted with pentane. The pentane was evaporated, under reduced pressure, from the extract to give a viscous yellow oil (188). Yield, 0.06g (5%). The n.m.r. spectrum had τ = 2.36 (multiplet, base = 16 cps), τ = 2.93 (multiplet, base = 36 cps), τ = 4.01 (singlet with signs of splitting, base = 8 cps), τ = 6.09 (singlet), τ = 6.16 (singlet), τ = 7.27 (singlet), all three singlets from a common base, 20-22 cps broad, and τ = 7.95 (multiplet, base = 12-14 cps). The ratio of the peak integrations was approximately 1:5:3:8:2 respectively, for each group of signals. An inspection of the n.m.r. spectrum showed that the signals at τ = 2.93, τ = 4.01, and τ = 7.27 were much stronger than those in the remainder of the spectrum. They were assigned as aromatic H, vinyl H, and methoxyl H, respectively. Compared with these by inspection the signals at τ = 2.36 and at τ = 6.09 were relatively weak.

45. Low Temperature Cycloaddition of Acetylene to Maleic Anhydride and Related Compounds

(General Technique)

The preparations were carried out after Koltzenberg and his co-workers.[13]

The irradiation apparatus (Diagram 38) used was of all Pyrex glass construction, and consisted of a methanol-cooled lamp-probe (1) sealed into an outer Pyrex jacket (2) which contained the solution to be photolysed.

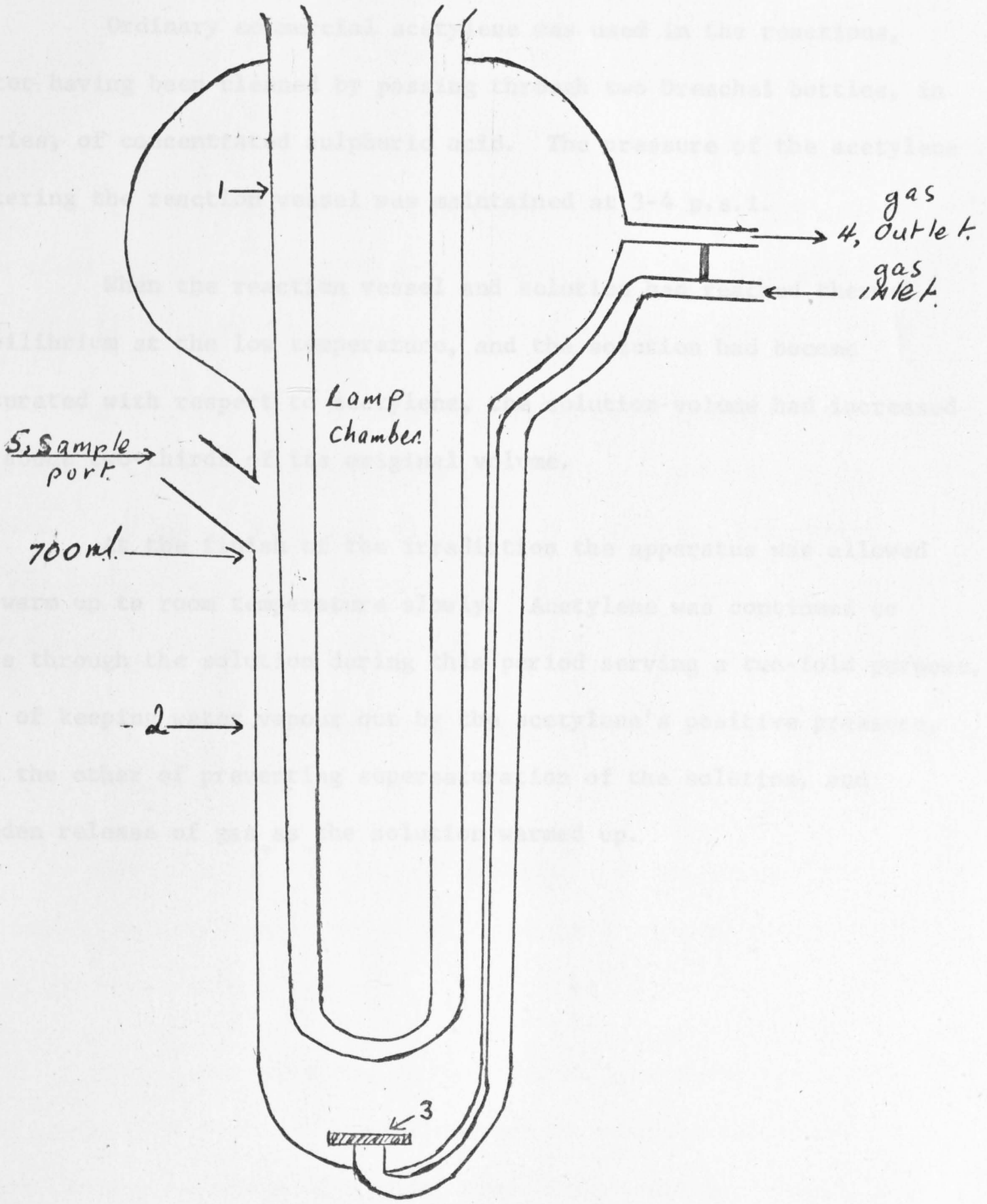
At the base of the outer jacket was a gas inlet with a sintered glass bubbler (3). Near the top of the outerjacket was the gas outlet (4). A sample port was positioned on the opposite side (5). The nominal solution-volume of the vessel was 700 ml.

The U.V. lamp used in the irradiation was a Philips 75 watt street-lamp with the envelope removed.

The methanol required to cool the probe was refrigerated to -30° in an external reservoir by a Thermostatic Refrigerator Type T.K.1, (Rheinische Buchs S.G., Switzerland) and pumped through the probe (1).

Major cooling of the apparatus and solution was done by immersing the glass vessel for two-thirds of its length in ethanol

DIAGRAM 38



which was maintained at -65^{o} in a "Minus Seventy" Thermostat Bath, Bridge Control Model, supplied by Townson and Mercer.

Ordinary commercial acetylene was used in the reactions, after having been cleaned by passing through two Dreschel bottles, in series, of concentrated sulphuric acid. The pressure of the acetylene entering the reaction vessel was maintained at 3-4 p.s.i.

When the reaction vessel and solution had reached thermal equilibrium at the low temperature, and the solution had become saturated with respect to acetylene, the solution-volume had increased by about two-thirds of its original volume.

At the finish of the irradiation the apparatus was allowed to warm up to room temperature slowly. Acetylene was continued to pass through the solution during this period serving a two-fold purpose, one of keeping water vapour out by the acetylene's positive pressure, and the other of preventing supersaturation of the solution, and sudden release of gas as the solution warmed up.

46. Preparation of Cyclobut-3-Ene-1,2-Dicarboxylic Anhydride (89)

Maleic anhydride (27) (10g) and benzophenone (111) (6g) were dissolved in acetone (300 ml) and irradiated in the presence of acetylene (71) according to the general procedure described.

A sample of the solution was taken at 53 hours. The solvent was removed from the sample and a n.m.r. spectrum run on the residue. The maleic anhydride vinyl H at τ = 2.98 had disappeared, and two new peaks at τ = 3.56 and τ = 5.96 had appeared. The benzophenone (aromatic H) remained at about τ = 2.48.

The irradiation was stopped and the apparatus allowed to warm up to room temperature.

The solution was filtered quickly, and the acetone and residual acetylene removed by evaporation under reduced pressure (20mm) at room temperature.

The acetone-free residue was extracted several times with small amounts of n-hexane until there was no benzophenone remaining in the residue as evidenced by thin layer chromatography. The R_f's of benzophenone, maleic anhydride and the compound (89) on silica gel in benzene were 0.2, 0.48 and 0.54 respectively. Iodine was used to develop the spots.

The remainder of the residue was then taken up quickly in clean dry chloroform, and filtered. The filtrate was evaporated down under reduced pressure, until syrupy, when n-hexane was added slowly with mixing. The resulting precipitate was filtered off, and washed with small amounts of cold n-hexane.

The material was recrystallised from chloroform/n-hexane, or alternatively, from ether, and then sublimed at 40^{o} (bath)/0.5mm.

The colourless crystalline compound, cyclobut-3-ene 1,2-dicarboxylic anhydride (89), was obtained. Yield, 6g (48.5%); melting point 88^{o} (literature, 90^{o}).

The infra-red spectrum had main bands ν_{max}: 1850w, 1750s, 1200s, 1140m, 1070s, 925m, 910s, 895s, 855s, 730s, and at 685s cm^{-1}. The n.m.r. spectrum showed τ = 3.42 (2H, singlet, vinyl H), and τ = 5.93 (2H, singlet, tertiary H).

47. Preparation of 1,2-Dimethyl-Cyclobut-3-Ene-1,2-Dicarboxylic Anhydride (91)

Dimethyl maleic anhydride (44) (6g), and benzophenone (111) (4g) were dissolved in acetone (300 ml), and irradiated in the presence of acetylene (71), according to procedure described.

After about 54 hours irradiation was stopped, and the solution was treated as described in the extraction procedure of the compound (89), Section 5(46).

The colourless crystalline compound, 1,2-dimethyl-cyclobut-3-ene-1,2-dicarboxylic anhydride (91), was obtained. Yield, 26g (43%); melting point 94°. (Found: C, 62.8; H, 5.5; O, 31.4%. C_8H_8O requires: C, 63.2; H, 5.3; O, 31.6%.)

The infra-red spectrum of the compound had main bands at ν_{max}: 1840w, 1775s, 1230s, 1130m, 1090m, 970s, 810s, 790s and 725s cm^{-1}. The n.m.r. spectrum had τ = 3.54 (2H, singlet, vinyl H), and τ = 8.54 (2H, singlet, 2 methyl H).

48. Preparation of N-Benzyl-Cyclobut-3-Ene-1,2-Dicarboximide (83)

N-benzyl-maleimide (84) (10g) and benzophenone (111) (6g) dissolved in acetone (300 ml) were irradiated for 63 hours in the presence of acetylene (71) in the manner described for (89), Section 5(46).

After about 63 hours the N-benzyl maleimide (84) had been fully reacted according to n.m.r. monitoring of the vinyl protons. After equilibrating to room temperature, the acetone solution was filtered, and the solvent and residual acetylene carefully evaporated off under reduced pressure at room temperature. The residue was extracted several times with n-hexane until most of the benzophenone was gone from the residue as evidenced by thin layer chromatography. The R_f's of benzophenone, n-benzyl maleimide, and the compound (83), in ether/n-hexane (1:1 by volume) on silica gel were 0.75, 0.30, and 0.01 respectively. Iodine was used to develop the spots. There were two unidentified fluorescent spots at R_f 0.7 and R_f 0.52.

The remainder of the residue (10g approx.) was adsorbed onto silica gel and added to a column of silica gel (200g) standing in hexane. A Paton Fraction Collector was used for the chromatography, collecting fractions of 15 ml volume.

The column was washed with n-hexane (300 ml), and then ether/n-hexane (1:10 by volume) solution was used for development. All residual benzophenone, and the two unidentified fluorescent substances were eluted, and the eluting solution changed to ether/n-hexane (1:3 by volume). 2,700 ml of this solution was used to elute compound (83).

The chromatography of the mixture was monitored by thin layer chromatography on silica gel in ether/n-hexane (1:1 by volume), using ultraviolet light, and iodine in order to examine the spots.

The solvent was evaporated off under reduced pressure, and several recrystallisations of the residue gave, N-benzyl-cyclobut-3-ene-1,2-dicarboximide (83). Yield, 6.7g (57%); melting point, 99°. (Found: C, 73.6; H, 5.2; 0, 15.9; N, 7.1%. $C_{13}H_{11}O_2N$ requires: C, 73.3; H, 5.2; 0, 15.0; N, 6.6%.)

The infra-red spectrum of the compound had main bands at ν_{max}: 1685s, 1340m, 1155s, 935m, 890m, 835m, 750m, and at 700s cm^{-1}. The n.m.r. spectrum had at τ = 2.72 (5H, singlet, phenyl H), τ = 3.58 (2H, singlet, vinyl H), τ = 5.49 (2H, singlet, methylene H), and τ = 6.21 (2H, singlet, tertiary H).

The ultraviolet spectrum showed end-absorption about λ_{max} = 210 mμ .

The compound was heated in a sealed tube at 300° for 15 minutes with slight darkening in colour. Examination of the ultraviolet spectrum of the pyrolysate showed no change in the compound (83).

49. Preparation of N-Phenyl-Cyclobut-3-Ene 1,2-Dicarboximide (138)

Aniline (139) (64mg) in dry ether (1 ml) was added slowly, in dropwise fashion to cyclobut-3-ene-1,2-dicarboxylic anhydride (89)

(100mg) in dry ether (3 ml). The solution was kept cold (ice-bath) and under a nitrogen atmosphere. After two hours a colourless crystalline precipitate formed, and the solution was left overnight. The ether was decanted from the crystals of N-phenyl-cyclobut-3-ene 1,2-dicarboxamic acid (140), which were washed twice with minimum amounts of ether and dried.

The compound (140) was dissolved in acetic anhydride (5 ml) and left, in a stoppered flask, at room temperature for about 72 hours.

The acetic anhydride was evaporated off under reduced pressure on a 70° water bath. The residue remaining was recrystallised several times from ethanol, and ethanol/water, to give N-phenyl-cyclobut-3-ene 1,2-dicarboximide (138). Yield, 42mg (26%); melting point, 144°. (Found: C, 72.0; H, 4.5; O, 16.1; N, 6.9%. Required for $C_{12}H_9O_2N$: C, 72.4; H, 4.6; O, 16.1; N, 7.0%.)

The infra-red spectrum had main bands at ν_{max}: 1760w, 1695s (imide), 1500m, 1240m, 1170s, 1040m, 925m, 870m, 790s, 765m, 730s, and at 690s cm^{-1}.

The n.m.r. spectrum had τ = 2.65 (5H, multiplet, 30 cps across base, aromatic H), τ = 3.42 (2H, singlet, vinyl H), and τ = 6.03 (2H, singlet, tertiary H).

The ultraviolet spectrum showed end-absorption at λ_{max} = 210 mμ .

The compound was heated in a sealed tube to 300° for 15 minutes with slight darkening. Examination of the ultraviolet spectrum of the pyrolysate showed no change in the compound (138).

50. Preparation of N-Phenyl-Cis-1,2-Dimethyl-Cyclobut-3-Ene 1,2-Dicarboximide (141)

Aniline (139) (64mg), in ether (1 ml), was added to cis-1,2-dimethyl-cyclobut-3-ene-1,2-dicarboxylic anhydride (91) (100mg), in ether (3 ml), and the procedure, described in Section 5(49) followed to give N-phenyl-cis-1,2-dimethyl-cyclobut-3-ene 1,2-dicarboximide (141). Yield, 57mg (37%); melting point 110°. (Found: C, 73.6; H, 5.9; O, 14.5; N, 5.8%. $C_{14}H_{13}O_2N$ requires: C, 74.0; H, 5.8; O, 14.1; N, 6.1%.)

The n.m.r. spectrum had τ = 2.60 (5H, multiplet, aromatic H), τ = 3.50 (2H, singlet, vinyl H), and τ = 8.5 (6H, singlet, methyl H).

The infra-red spectrum had main bands at ν_{max}: 1760w, 1700s (imide), 1490m, 1275m, 1240m, 1140s, 950m, 800m, 770m, 730s, 710s, and at 680s cm^{-1}.

The ultraviolet spectrum of the compound (141) showed end absorption at λ_{max} = 210 mμ .

The compound was heated in a sealed tube at 240° for 15 minutes with slight darkening in colour. Examination of the ultra-violet spectrum of the pyrolysate showed no change in the compound (141).

51. Attempted Preparation of N-Benzyl-Cis-1,2-Dimethyl-Cyclobut-3-Ene-1,2-Dicarboximide (143)

Benzylamine (182) (70mg), in ether (1 ml), was added to cis-1,2-dimethyl-cyclobut-3-ene dicarboxylic anhydride (91) (100mg), in ether (3 ml), and the procedure described in Section 5(49), followed to give, after removal of the acetic anhydride, a colourless, syrupy liquid.

An n.m.r. spectrum of the liquid had τ = 2.71 (5H, singlet, aromatic H), τ = 3.61 (2H, singlet, vinyl H), τ = 5.38 (2H, singlet, methylene H), and τ = 8.65 (6H, singlet, methyl H), and also τ = 5.51, τ = 8.61, and τ = 7.95.

(No further examination has been made.)

52. Preparation of N-Phenyl-1,6-Dimethyl-7,8-Diphenyl-Tricyclo ($4,2,1,0^{2,5}$) Nona-7-Ene-9-One 3,4-Dicarboximide (144)

1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one 3,4-dicarboxylic anhydride (90) (0.35g), and aniline (139) (80mg) were dissolved in 2-ethoxyethanol (5 ml), and gently refluxed, under anhydrous conditions, overnight.

On cooling, the solution was poured into water (200 ml) and well-mixed. The mixture was extracted with ether (50 ml × 3) and the combined ether extracts washed with water (10 ml × 3), dried with sodium sulphate and filtered.

The ether was evaporated off under reduced pressure, and the solid residue remaining was recrystallised, several times from ether/n-hexane, to give N-phenyl-1,6-dimethyl-7,8-diphenyl-tricyclo ($4,2,1,0^{2,5}$) nona-7-ene-9-one-3,4-dicarboximide (144). Yield, 0.26g (59%); melting point, 226° (decomp). (Found: C, 79.5; H, 5.6; O, 12.1; N, 3.1%. $C_{31}H_{25}O_2N$ requires: C, 81.0; H, 5.5; O, 10.5; N, 3.1%.)

The infra-red spectrum had main bands at ν_{max}: 1810w, 1765s, 1710s, 1500m, 1190s, 1160s, 1110m, 760m, 700s, and at 690s cm^{-1}.

The n.m.r. spectrum had τ = 2.76 (12H, multiplet, aromatic H), τ = 6.92 (2H, multiplet, base = 9 cps, cyclobutyl H), τ = 7.09 (2H, multiplet, base = 9 cps, cyclobutyl H), and τ = 8.62 (6H, singlet, methyl H).

53. Irradiation of 2-Methyl-1,4-Naphthoquinone (1) and Cyclohexene (148)

2-methyl-1,4-naphthoquinone (25g, 0.0145M) and cyclohexene (0.2g, 0.029M) were dissolved in benzene (100 ml), and irradiated under an atmosphere of nitrogen with a battery of four Philips' 18 inch, 15 watt Blacklight lamps for 4 to 6 weeks. The benzene was evaporated off under reduced pressure, and the brown, syrupy residue chromatographically fractioned on silica gel column (3.50g) using a Paton Fraction Collector. The size of each fraction collected was 15 ml.

The column was first developed with n-hexane (1 litre) then with ether/n-hexane solution (1:19 by volume, 1 litre) followed by development with ether/n-hexane (1:9 by volume, 3 litres).

This latter solvent system eluted a golden yellow oil (176). Yield, 1g (38%).

The infra-red spectrum had main absorptions at ν_{max}: 1680s, 1600s, 1300s (broad) to 1250s, 1160m, 790m, 950m, 780m, 760m, and at 720m cm^{-1}. The n.m.r. spectrum had τ = 1.93 (multiplet, base = 18 cps, aromatic H), τ = 2.28 (multiplet, base = 18 cps, aromatic H), τ = 3.17 (1H, quartet, J = 3 cps, vinyl H), τ = 7.15 (1H, multiplet, base = 14 cps, methine H), τ = 7.8 (3H, doublet, J = 3 cps, methyl H), τ = 8.5 ± 0.5 (7H, complex multiplet, cyclohexyl H).

54. Irradiation of 2-Methyl-1,4-Naphthoquinone (1) and But-2-Yne (160)

2-methyl-1,4-naphthoquinone (1) (2.5g, 0.0145M), and but-2-yne (160) (0.15g, 0.029M) were dissolved in benzene (100 ml), irradiated as described in Section 5(53), and chromatographically fractioned as described in Section 5(53).

The ether/n-hexane (1:9 by volume) solvent system (3 litres) eluted material, which on recrystallisation several times from n-hexane, and then sublimation at 60°/0.5mm gave the compound (151). Yield,

1.95g (75%), melting point 90-91°. (Found: C, 78.6; H, 6.5; O, 14.7%. Required: C, 79.6; H, 6.2; O, 14.1%.)

The n.m.r. had τ = 1.90 (multiplet, base = 18 cps, aromatic H), τ = 2.20 (multiplet, base = 18 cps, aromatic H), τ = 6.50 (1H, multiplet, base = 12 cps, methine H), τ = 8.38 (3H, apparent singlet, methyl H), and τ = 8.48 (6H, apparent singlet, vinyl methyl H). Both signals at τ = 8.38 and τ = 8.48 had a common base of 16 cps. The infra-red spectrum has main bands at ν_{max}: 1675s, 1590s, 1290s, 1250s, 1120m, 970m, 910m, 840m, 800m, and at 730s cm^{-1}.

The n.m.r. spectrum of the compound (151) remained unchanged after the compound had been heated at 260° for 30 minutes.

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